PECAN OIL EXTRACTION WITH BATCH STATIC AND CONTINUOUS FLOW SUPERCRITICAL CARBON DIOXIDE

By

CHAO ZHANG

Bachelor of Science

in Mechanical Engineering

East China University of Chemical Technology

Shanghai, China

1986

Submitted to the Faculty of the
Graduate College of the
Oklahoma State University
in partial fulfillment of
the requirements for
the Degree of
MASTER OF SCIENCE
December, 1994

PECAN OIL EXTRACTION WITH BATCH STATIC

AND CONTINUOUS FLOW SUPERCRITICAL

CARBON DIOXIDE

Thesis Approved:

Gerald Brusewitz

Thesis Adviser

Glenn Kranzler

Nils A. Maness

Thomas C. Collins

Dean of Graduate College

ACKNOWLEDGMENTS

I wish to express my sincere appreciation to my major adviser, Dr. Gerald H. Brusewitz for his constant guidance and support in the completion of this study. I would also like to express my gratitude to Dr. Niels O. Maness and Dr. Glenn A. Kranzler, members of the advisory committee, for the assistance and encouragement. They offered much needed advice in experimental design, instrument operation and data statistical analysis. Their assistance to my test and to the thorough editing and proof reading of my thesis were very helpful.

Thanks also extend to the staff and students of the Horticulture Department and Chemical Engineering Department for their assistance to this study.

A special thanks is to the Agricultural Engineering Department for offering me this study opportunity in the United States and for their friendship provided in the various phases of this study.

Finally, I would like to express my gratitude and thanks to my parents and my wife for their love, sacrifice, understanding, support and encouragement.

TABLE OF CONTENTS

Chapter Page

I. INTRODUCTION 1

II. LITERATURE REVIEW 3

Composition of the Pecan Kernel 3
Components of Pecan Kernel Quality 4
Conventional Storage Methods 5
Solvent Extraction 8
Supercritical Fluid Extraction 8
The Properties of Carbon Dioxide 10

III. MATERIALS, EQUIPMENT, AND METHODS 12

Pecan Kernels 12
Equipment 12
Batch Static Extraction System 12
Continuous Flow SCFE System 14
Extraction Procedures 16
Batch Static Extraction with Gaseous CO_2 16
Continuous Flow Supercritical Extraction 17

IV. RESULTS AND DISCUSSION 20

Static Extraction Experiments 20
Pecan Weight Loss 20
Pecan Kernel Condition 26
Continuous Flow Supercritical Fluid Extraction 33
Preliminary Tests 33
Main Tests 36
Pecan Color 42

V. CONCLUSIONS AND RECOMMENDATIONS 46

Conclusions 46
Recommendations for Further Study 47

REFERENCES 49

APPENDIX 53

A. UNDER PRESSURE TIME EFFECT ON PECAN OIL EXTRACTION WITH STATIC CO2 (DATA FOR FIGURE 5) 54
B. PRESSURE RELEASE TIME EFFECT ON THE PECAN FINAL WEIGHT LOSS (DATA FOR FIGURE 6) 55
C. TIME UNDER PRESSURE EFFECT ON THE UNBROKEN PECAN KERNELS (DATA FOR FIGURE 7) 56
D. PRESSURE AND TIME EFFECT ON THE OIL RECOVERED AT 40 °C (DATA FOR FIGURE 9) 57
E. PRESSURE AND TIME EFFECT ON THE OIL RECOVERED AT 80 °C (DATA FOR FIGURE 10) 58
F. PECAN FINAL WEIGHT LOSS AFTER 160 MIN AS A FUNCTION OF PRESSURE AT 40 AND 80 °C (DATA FOR FIGURE 11) 59
G. EXPERIMENT I; 17.7 MPa, 40 °C, 160 min, 250-500 ml/min 60
H. EXPERIMENT II; 21.3 MPa, 40 °C, 160 min, 250-500 ml/min 61
I. EXPERIMENT III; 41.3 MPa, 40 °C, 160 min, 1200 ml/min 62
J. EXPERIMENT IV; 55.1 MPa, 40 °C, 160 min, 1200 ml/min 63
K. EXPERIMENT V; 55.1 MPa, 40 °C, 160 min, 250-500 ml/min 64
L. EXPERIMENT VI; 55.1 MPa, 40 °C, 160 min, 250-1200 ml/min 65
M. EXPERIMENT VII; 68.9 MPa, 40 °C, 160 min, 1200 ml/min 66
N. EXPERIMENT VIII; 17.7 MPa, 80 °C, 160 min, 250-500 ml/min 67
O. EXPERIMENT IX; 21.3 MPa, 80 °C, 160 min, 250-500 ml/min 68
P. EXPERIMENT X; 21.3 MPa, 80 °C, 160 min, 250-500 ml/min 69
Q. EXPERIMENT XI; 21.3 MPa, 80 °C, 160 min, 1200 ml/min 70
R. EXPERIMENT XII; 41.3 MPa, 80 °C, 160 min, 1200 ml/min 71
S. EXPERIMENT XIII; 55.1 MPa, 80 °C, 160 min, 1200 ml/min 72
T. EXPERIMENT XIV; 55.1 MPa, 80 °C, 160 min, 250-500 ml/min 73
U. EXPERIMENT XV; 68.9 MPa, 40 °C, 160 min, 1200 ml/min 74

LIST OF TABLES

Table		Page
I.	Static Gaseous CO_2 Pressure And Temperature Effects On The Pecan Oil Extraction	24
II.	Pecan Final Condition After Three Hours Extraction	29
III.	Pecan Final Condition After One Hour Extraction	30
IV.	Pecan Final Condition *Vs* Final Weight Loss	34
V.	Pecan Final Weight Loss And Oil Collected In Vial At Low CO_2 Flow Rate	35
VI.	Pecan Final Weight Loss And Oil Collected In Vial At High CO_2 Flow Rate	37
VII.	Oil Recovered At Different Extraction Temperatures And Pressures	41
VIII.	Linear Regression Equations For Oil Recovery *Vs* Time	41
IX.	"L*, a*, b*" Color For Pecan Halves Before And After Oil Extraction	45

LIST OF FIGURES

Figure Page

1. Schematic Of Batch Static CO_2 Extraction System 13

2. Schematic Of Continuous Flow SCFE System 15

3. Static CO_2 Temperature Effect On The Pecan Final Weight Loss 21

4. Static CO_2 Pressure Effect On The Pecan Final Weight Loss 22

5. Under pressure Time Effect On Pecan Oil Extraction With Static Gaseous CO_2 25

6. Pressure Release Time Effect On The Pecan Final Weight Loss 27

7. Time Under Pressure Effect On The Unbroken Pecan Kernels 31

8. Pecan Weight Loss *Vs* Unbroken Kernels 32

9. Pressure And Time Effect On The Oil Recovered At 40 °C 39

10. Pressure And Time Effect On The Oil Recovered At 80 °C 40

11. Pecan Final Weight Loss After 160 min As A Function Of Pressure At 40 And 80 °C 43

CHAPTER I

INTRODUCTION

The pecan is a major edible tree nut of America. It ranks among the leading horticultural crops in the Southern United States. Although output is influenced by the alternate annual bearing pattern of pecan trees, the total U. S. production averages about 280 million pounds with a value of about $238 million. The 1993 crop was estimated by USDA to be 364 million pounds (Wise, 1993). The increased use of pecans by food manufacturers and consumers has resulted in a steady increase in the proportion of shelled pecans, which amounts to about 85% of the total crop. The remaining 15% of the nuts are sold in the shell (Rosengarten, 1984). Shelling reduces the weight of pecans by about 64% and the volume by 50%, and reduces storage volume and costs. At the same time, shelling reduces the storage life of pecans by making them more susceptible to rancidity and off-flavors (Woodroof, 1979).

The short kernel shelf life partially limits the development of an expanded pecan market and results in price fluctuations (Florkowski and Xi-Ling, 1990).

The main cause of off-flavors in pecan nuts during storage is the susceptibility of lipids to oxidative deterioration of the lipids. The stability of lipids is closely related to the content of unsaturated fatty acids. The oxidative rancidification of its unsaturated fatty acids causes the pecan nuts to be extremely susceptible to quality deterioration during

storage. The higher the content of lipids, the greater the potential for reaction with oxygen and thus the formation of rancidity. Pecan kernels, which contain about 70% lipids with a high percentage of unsaturated fatty acid, show considerable flavor instability (Cruess and Armstrong, 1947).

To extend the shelf-life of pecans, research has been directed at developing processing and storage methods to maintain the quality of pecan kernels during storage (Forbus et al., 1983 b). Research in another direction investigated the potential to partially extract pecan oil with a solvent such as hexane to extend the shelf-life of pecan kernels (Waters and Knight, 1986). Extracting oil from pecans with a solvent has the advantage of being done without damaging the kernels but has the disadvantage that solvent-soluble vitamins and other materials are removed from the meal. Organic solvents have now become expensive and their possible escape from the extraction system is a potential source for atmospheric pollution and an explosion hazard. Recently, the use of supercritical carbon dioxide (SC-CO_2) for the fractionation of organic materials is receiving increasing attention.

This study was conducted to determine the feasibility of partial extracting oil from pecans with SC-CO_2. The specific objectives were as follows:

1. To identify the important parameters which determine significant extraction, using SC-CO_2, of oil from pecan kernel halves.

2. To determine the yield of oil from pecans, when extracted by static and continuous flow SC-CO_2, as functions of the process temperature, pressure, and time.

CHAPTER II

LITERATURE REVIEW

Composition of the Pecan Kernel

Pecan quality and changes in quality after harvest are dictated by the chemical composition of the kernels. Pecan kernels are especially susceptible to staleness and oxidative rancidity because of their high oil contents.

Lipids (oils) make up the largest single component of the pecan kernel (Kays, 1987). The concentration of lipids ranges from 55 to 75%, by weight, among varieties. Pecan oil is a mixture of fatty acids. Twenty three fatty acids have been identified in the oil from the pecan. Of these fatty acids, unsaturated fatty acids predominate with oleic (one double bond) and linoleic (two double bond) making up about 84%. There is a positive correlation between the concentration of linoleic acid (two unsaturated positions) and the rate of development of rancidity. It appears that the greater the degree of unsaturation, the more susceptible the nut is to oxidation and rancidity. In addition to lipids, pecan kernels also contain 12-15% carbohydrate, 9-10% protein, 3-4% moisture and approximately 1.5% minerals (Kays, 1987; Stein, 1980).

Tocopherols are the most important natural antioxidants in fats and oils of pecans. Fourie and Basson (1989) found that pecan nuts, which contained less total tocopherols

(about 20 mg/100g) and decreased their content during storage, became rancid after four months storage.

Components of Pecan Kernel Quality

The quality of pecan kernels is governed by several factors which considered collectively determine the acceptability of the pecan to the consumer. The primary components of quality which are the most susceptible to losses during storage are color, flavor, degree of intactness of the kernels, and the absence of insects and diseases (Kays, 1987).

The color of pecan kernels, although is not always a precise index of the kernel quality, is commonly used as a primary measure of the overall quality of the kernel (Kays, 1979). Quality deterioration of pecan kernels is often accompanied by a darkening of their color which influences processors and consumers to associate light colored kernels with desirable quality. Consumer preference for light colored kernels and the ease and accuracy with which color can now be measured with automated electronic color sorting equipment has increased the emphasis placed on kernel color (Kays, 1987). The inherent color differences among cultivars, processing methods, storage time, and conditions can produce significant differences in the appearance of pecan kernels (Forbus et al., 1983 a).

Fresh pecans have a distinctive, pleasing taste and odor. The volatile aroma of pecan kernels is due to low weight molecular alcohol and aldehydes (Stein, 1980). Chemical changes may occur during storage under improper conditions and pecans can become rancid and unappetizing. Because of the general lack of understanding of pecan

flavor chemistry, there are no objective measures of flavor quality, hence the absence of standards (Kays, 1987).

Shelled pecans are graded into half-kernels, pieces and particles, and dust based on size and the degree of intactness of the kernel (USDA, 1969). Half-kernels are the individual halves of the nut which have no more than one-eight of its original volume missing. The size of individual kernels and pieces of kernels has a significant influence on the value of pecans.

Insects and diseases can pose serious quality problems for storage and marketing of pecan kernels. However, with proper storage conditions pecans can be kept free of these threats.

Conventional Storage Methods

One of the most effective ways of retarding rancidity in pecans is by refrigeration. They can be held from one season to the next by storing at 0 °C with 70 to 75% relative humidity. At 10 °C they remain good for six months, and at 21 °C for about four months. Kernel quality can be maintained for up to three years at temperatures of -2 °C and below (Woodroof and Heaton, 1961). The nuts must be harvested in the fall and stored before oil begins to leak out of the kernels or staleness begins. When pecans are used as condiments by food processors, refrigeration is used to maintain the high quality of the ingredients in their products.

However, at the retail level this protection is usually not provided for shelled kernels and maintaining quality is dependent on the material in which they are packaged. Often, this material offers more display appeal than preservation characteristics.

A second method of retarding rancidity is by excluding air. This may be done by (a) the use of hermetically sealed containers; (b) packing under vacuum; (c) replacing the air in containers with inert gases such as nitrogen or hydrogen; or (d) coating the nuts with collodion or water glass. Syrups and sugar coatings are fairly effective in excluding oxygen (Cruess and Armstrong, 1947). By reducing the O_2 exposure to the nuts, the storage life may be extended by as much as two or three times.

A third method of retarding rancidity in pecans is by the use of antioxidants such as citric acid, propyl gallate (Godkin et al., 1951) and acetylated monoglycerides (Senter and Forbus, 1979). Fresh pecans contain about 0.45% tocopherol, a naturally occurring antioxidant, which renders pecans quite stable for a while, depending largely on the temperature. Adding antioxidants to slightly aged pecans is of more value because the natural antioxidants now have partially been lost.

Woodroof and Heaton (1961) and McGlammery and Hood (1951) reported that pecan meats heated to 80 °C in dry air or oil doubled their self-life by inactivating oxidative enzymes. Heating to higher temperatures darkened the kernels and produced a slightly cooked flavor. Heating pecan meats by dry roasting or with infrared heat rays to 185 °C for 15 min., destroys natural antioxidants but increases many times the aroma and flavor. Fine grinding roasted pecan meats and placing in jars to exclude air, but without refrigeration, increased the storage life by 20 times more than those without the treatment.

Freshness was extended even longer with the addition of antioxidant or use of refrigeration.

A four-minute steam conditioning process of inshell pecans and a one-minute dielectric heating treatment of shelled kernels were found to be equally effective in improving the storage stability of pecan kernels during accelerated storage simulating typical marketing conditions (Forbus et al., 1983 b).

Other methods of retarding rancidity in pecan meats include storing in the dark and using containers coated on the inside with an antioxidant. It has been established that storage life of nuts and oils can be extended by the addition of antioxidants such as BHA, BHT, and propyl gallate. These antioxidants, used with nuts and oils or fat containing foods, present problems such as partial effectiveness with highly unsaturated oils, discoloration with metals, odors (particularly associated with phenolic type antioxidants), and poor solubility.

For more complete control of rancidity in pecans and pecan meats one or more of the following procedures should be followed: (a) Dry kernels to 4.5% moisture as soon as possible after harvest using circulated air not higher than 38 °C. (b) Store at 3 °C or lower, with 65% relative humidity air for in-shell pecans. (c) Heat to 80 °C for 2 min. to inactivate oxidative enzymes. (d) Reduce oxygen in the atmosphere by placing under vacuum, or in 98% nitrogen or carbon dioxide. (e) Treat nuts or nutmeats with 0.1% BHA (butylated hydroxyanisole), BHT(butylated hydroxytoluene), or NDGA antioxidant. (f) Coat nutmeats with sugar glaze, heavy syrup, zein, dextrins or collodion to partially

exclude air. (g) Pack in containers coated on the inside with BHA, BHT or NDGA antioxidant. (h) Exclude light by keeping in the dark or in amber colored containers.

Solvent Extraction

Solvent extraction (SE) is the commercial method now used for vegetable oil extraction. The process is carried out in a closed system using hot organic solvent. The oil/solvent mixture is separated from the meal, and the solvent is fractionated from both for re-use. Organic solvent, such as hexane has long been the preferred solvent for extracting oil from agricultural products. Recently, economic and social factors have caused government and industry to seek cheaper and safer solvents.

Supercritical Fluid Extraction

Supercritical fluid extraction (SCFE) is the substitution of a fluid in its supercritical (SC) state for hexane in the conventional solvent extraction process. It has been described as a combination of distillation, which separates on the basis of different vapor pressures, and solvent extraction, which relies on solubility as affected by molecular structure.

SCFE is conceptually the same as solvent extraction but the specialized equipment reaches the limits of engineering technology. Extractor vessels and plumbing to withstand the extreme pressures and yet provide practical residence volume and production are expensive. Small batch-type equipment can be fabricated but continuous flow apparatus requires designs uncommon to industrial experience (USDA, 1982).

The solvent must, to a certain extent, be miscible with the original mixture and must be capable of preferentially dissolving the component(s) being extracted. In the traditional extraction process, it is essential for the solvent to be a liquid, because of its high solvent power compared with the gas. However, supercritical fluids have the solvent power of liquids and better mass transfer characteristics (e.g. lower viscosity and higher diffusion coefficient) than typical liquids. Thus, interest in extraction with supercritical fluids has been growing rapidly in recent years. Solvents such as ammonia, ethylene, toluene and carbon dioxide all show promise for supercritical fluid extraction. Of these, CO_2 offers unique advantages. Carbon dioxide is abundant, non-reactive, non-toxic and environmentally harmless. Minor leaks or losses of fluid would be of little consequence. SC-CO_2 is miscible with vegetable oils (hydrocarbons) and it can induce partial miscibility in some hydrocarbon mixtures. Supercritical carbon dioxides can induce swelling (i.e. the volume of the carbon dioxide plus oil mixture is greater than that of oil alone) and reduces the viscosity of oils.

The most notable commercial application of supercritical carbon dioxide is in the coffee decaffeination process (INFORM, 1990; Goodrum and Kilgo, 1987 a; List et al., 1984 a; List et al., 1984 b). Other examples involving supercritical carbon dioxide are vegetable oil extraction (INFORM, 1990; Goodrum and Kilgo, 1987 b; List et al., 1984 a; List et al., 1984 b), recovery of peppermint and spearmint (Barton, 1992) and capsaicin (Knez, 1992), and fractional separation of marjoram leaves (Reverchon, 1992).

SC-CO_2 was used to replace hexane for the extraction of oil from dry-milled corn germ (Christianson et al., 1982). Oil yields were comparable to those obtained with

hexane. In comparing the SC-CO_2 extracted flours with hexane-extracted one, it was evident that SC-CO_2 was more effective than hexane both in reducing the total residual lipid level and in a tenfold reduction of the peroxide activity. SC-CO_2 extraction could denature peroxide enzymes, which are heat resistant, from food products.

The Properties of Carbon Dioxide

To properly use carbon dioxide as an extractive solvent, the properties of carbon dioxide must be well understood. When a gas is heated above its critical temperature, it cannot be liquefied, regardless of the pressure applied. As one applies increasing pressure, the density of the gas starts to increase and approaches that of a liquid. A gas which has been heated above its critical temperature and pressurized above its critical pressure is called a supercritical fluid. It has solvent properties approaching those of the liquid state, and high diffusivity and low viscosity resembling the gaseous state (Vukalovich and Altunin, 1968). By varying such parameters as temperature and pressure, selected components can be differentially extracted from a mixture, something like fractional distillation.

The critical temperature of carbon dioxide is 31.0 °C. This mild critical temperature determines the optimal performance of SC-CO_2 to be in the temperature range of 35 to 70 °C.

The solution property of SC-CO_2 is affected by the temperature and pressure Friedrich (1983). Above its critical pressure range of 7 to 41 MPa (1,000 to 6000 psi), CO_2 is quite compressible. The density, which is related to solute holding power, changes

rapidly in this range. Therefore, the expected increases in solubility with increases in temperature can be observed at the high pressure. At the lower pressures, the increased solubility effect due to temperature is overcome by the decrease in density and related decrease in solute holding power.

Supercritical carbon dioxide offers the advantage of being easily removable from the extracted oil. In contrast to organic solvents and some of their contaminating components, carbon dioxide is nontoxic, and it does not lead to environmental pollution. Moreover, this inexpensive gas is available in a virtually unlimited quantity both from renewable organic resources and from inorganic materials including various minerals. It is also a byproduct of various industrial processes.

CHAPTER III

MATERIALS, EQUIPMENT, AND METHODS

Pecan Kernels

Shelled pecan halves that had been cleaned and sized were obtained from a commercial source. Kernels with light color, distinctive and pleasing aroma and taste, free from diseases and insects, and absence of breakage were selected for oil extraction tests. The nutmeats had about 4% moisture content. Physical and chemical parameters indicative of quality, such as kernel moisture content, color, fatty acid compositions and oil content were measured before oil extraction tests. Initial oil content was 66% by weight of the whole kernel.

Equipment

Two different types of equipment were used for the batch static and continuous flow SCFE experimentation.

Batch Static SCFE System:

The schematic diagram of the batch static SCFE system is shown in Figure 1. Gaseous carbon dioxide of high purity was obtained from a 30-L storage tank. A

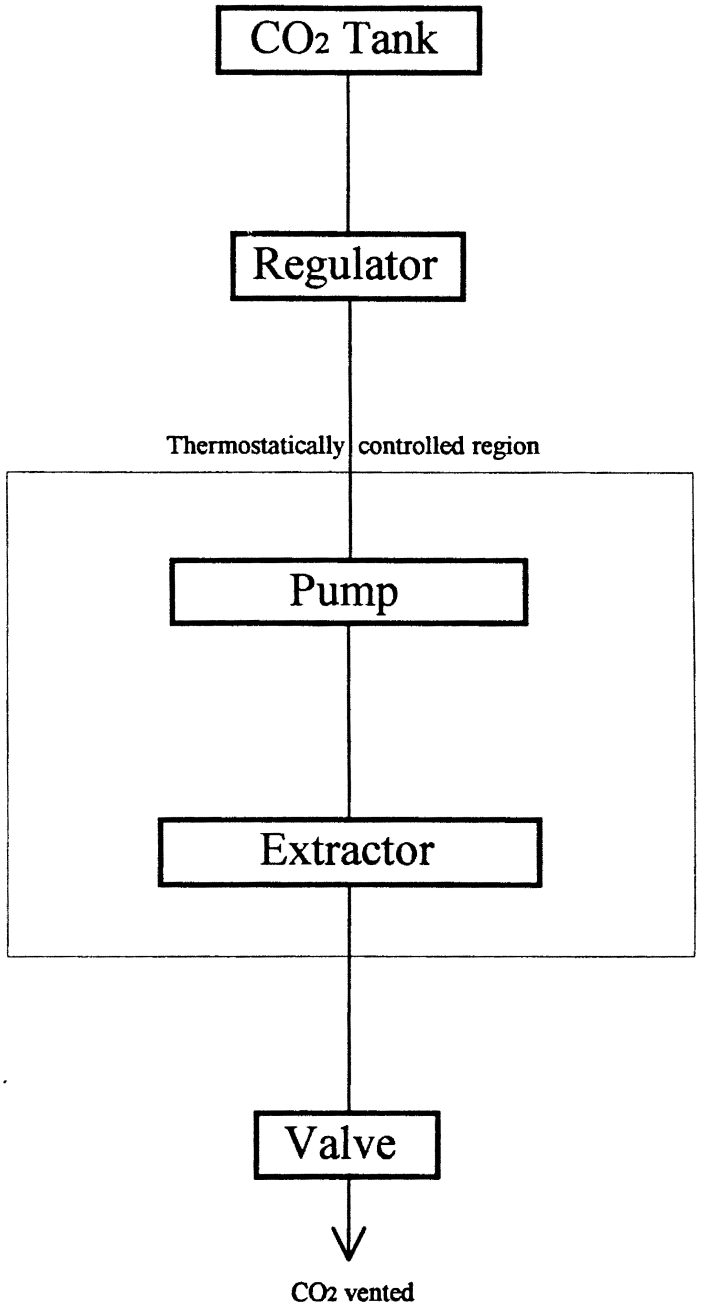

Figure 1. Schematic of batch static CO_2 extraction system.

regulator controls the pressure which is indicated by a manometer. A hand screw pump (RUSKA), increased the pressure of carbon dioxide and maintained steady pressure. A heating belt was tightly wrapped around the outside of the pump cylinder to heat the CO_2 to above its supercritical point.

The pressure used during extraction was adjusted by the hand pump and checked by a digital pressure transducer of 2000.0 psi capacity. The extractor, a horizontal high pressure cylinder vessel with 40 ml inside volume, was enclosed in a thermostatically controlled insulated casing (RUSKA).

Continuous Flow SCFE System:

A Dionex Model SFE-703 supercritical fluid extraction instrument was utilized for the continuous CO_2 flow pecan oil extraction experiment (Figure 2). This system is an automated, multi-cell off-line extraction instrument that can be operated in either automatic or manual mode. Methods for automatic operation are easily programmed and input with a front keypad.

Supercritical CO_2 is contained in a storage tank and the pressure is monitored at a manometer (pressure must be greater than 9 MPa). Nitrogen or compressed air for air valve and pump control (about 0.7 MPa) was supplied for operation of pneumatic systems (pump operation, oven and sample door operation, etc.). Temperature and CO_2 pressure are set to the desired value on the control panel. The compressed gas CO_2 flows through a manifold to assure thermal equilibrium before reaching the extraction cells. This unit is capable of extracting up to eight cells simultaneously using the same temperature and

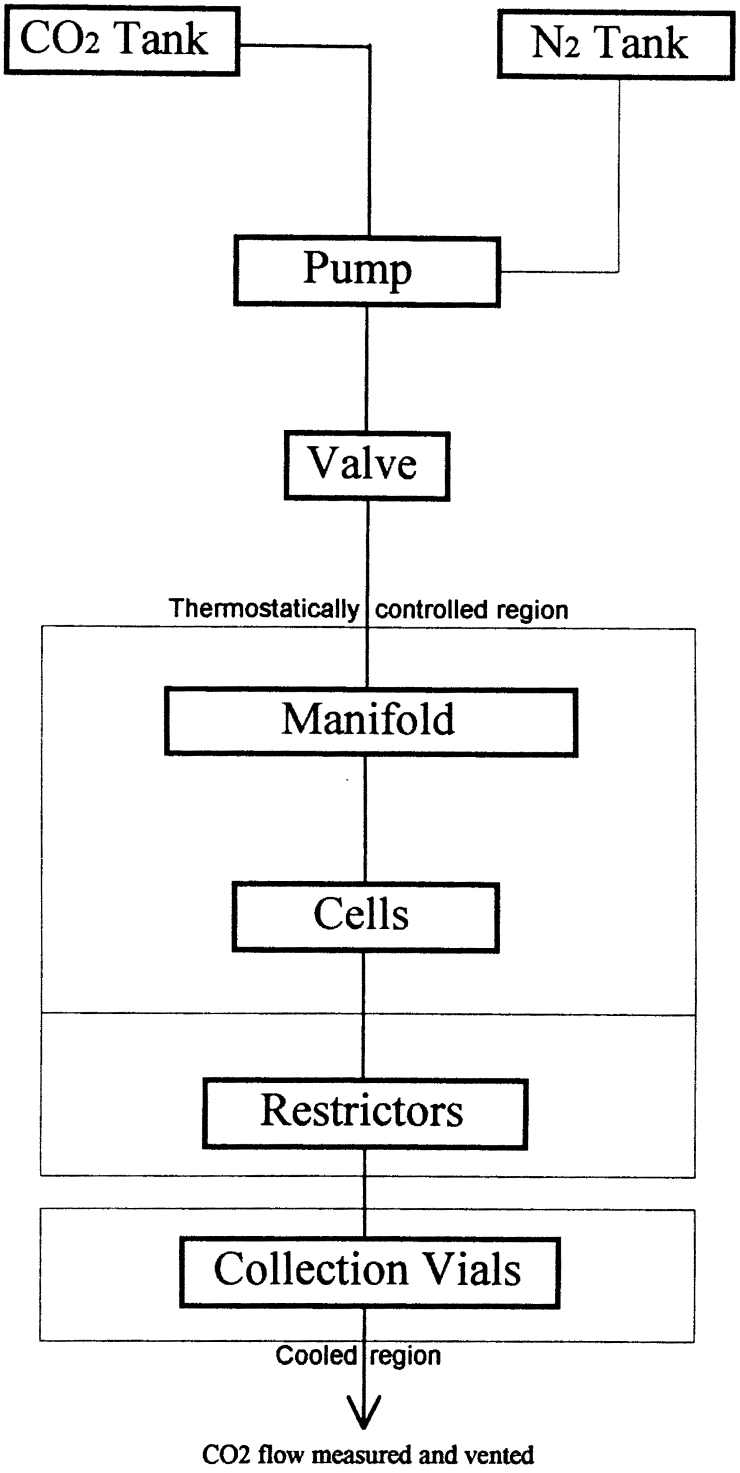

Figure 2. Schematic of continuous flow SCFE system.

pressure conditions for all cells. The 24 ml stainless steel extraction cells were rated at 68.9 MPa (10,000 psi) and installed in a temperature controlled oven chamber. The flow rate of CO_2 through the extraction vessel is regulated by the size of the restrictor. Flow was measured with electronic flow sensors for each cell and displayed in both instantaneous and cumulative time. Due to the sudden pressure drop that occurred in the oil collecting vial, the CO_2 and the oil separate in the receivers. The gas passes through a flow meter before being vented to the atmosphere.

Extraction Procedures

Batch Static Extraction with Gaseous CO_2:

Initial experiments were conducted using the batch static extraction system to determine the effect of CO_2 pressure and temperature on the removal of oil from the pecan kernel.

Pecan kernel halves (7-8 g) were wrapped in tissue paper, weighed and placed in the extraction cell. The CO_2 line was connected to the loaded extraction cell. Air was removed from the internal system by rinsing with carbon dioxide at a pressure of approximately 0.69 MPa (100 psi) for about five min. Then, the extraction cell inlet and vent valves were closed. Carbon dioxide was introduced from the CO_2 storage tank into the cylinder of the hand screw pump. The CO_2 storage tank connection valve was closed and the CO_2 pressure was increased by the pump. At the same time, heat from electrical resistance coils was added to the pump cylinder and extraction cell. When the desired temperature and pressure were reached, the inlet valve was opened and the extraction cell

was filled with carbon dioxide. The pump was used again to increase the inside cell pressure to the extraction pressure.

Extraction started by opening the extractor inlet valve. During the process the temperature and pressure of the CO_2 inside the extractor were monitored to insure that it was stable. After completion of the extraction process, the extraction cell vent valve was slowly, partially opened to release the carbon dioxide to the atmosphere. When the CO_2 pressure was released, most of the extracted pecan oil was adsorbed by tissue papers but part of the extracted oil was dissolved in the exhaust CO_2 stream. The pecan kernels and tissue papers were removed from the extractor and each was weighed. The change in pecan weight was computed and the kernels were observed for damage (cracked or broken).

Continuous Flow Supercritical Extraction:

Pecan kernel halves (about 5-6 g), were weighed and loaded into one to eight extraction cells, using glass wool plugs to retain the pecan in both ends of the cell. The filled cells were weighed, placed in the main oven cavity, and connected to the manifold and restrictors. The low CO_2 flow rate (250 ml/min.) and medium CO_2 flow rate (500 ml/min.) restrictors were assembled in alternate order for the preliminary experiments, and the high flow rate (1200 ml/min.) ones were used for main tests. The restrictors were heated to 150 °C to prevent the lipids from precipitating out in the small diameter tubing during decompression.

Glass wool was inserted into the inner tube and the inside of each collection vial to ensure complete trapping of pecan oil. When performing this procedure, it was found best to leave a space of approximately 2 cm between the glass wool and the upper end of the inner tube to allow penetration of the restrictor into the vial. Then, each vial was weighed and inserted into the vial rack.

Method parameters, extraction temperature and pressure, pressure steps, under pressure time, and restrictor temperature were input to the keyboard's edit menu, and the test was started. When extraction was completed, the system discharged any remaining CO_2 into the Teflon vent tubing leading to the atmosphere..

Data were collected every 20-60 min., according to the stop condition. Initially the time interval was short and as the experiment proceed, the time intervals were extended. Data collection consisted of recording the extraction pressure and temperature, vial and restrictor temperature, CO_2 flow rate and accumulated volume of total CO_2. The oil collection vials were removed for weighing of the amount of pecan oil collected at the selected time intervals. The extraction process was terminated after 160 min. and the loaded cells and pecan kernels were weighed again. The kernel final weight loss and the percentage of oil recovery for each time interval based on the percentage the initial oil in the pecan kernels were computed. The kernels were put into a freezer for color evaluation later.

Color measurements were taken of non-extracted pecan halves and samples after having continuous flow oil extraction tests. The hue, value, and chroma were determined with a Minolta Chroma Meter CR-300 using a 3-mm diameter viewing port on the optical

head. Fifteen halves per treatment were randomly selected for the color measurements. Four L*(lightness), a*(red), and b*(yellow) values were recorded on each pecan half by axially rotating the kernel 90° between readings.

CHAPTER IV

RESULTS AND DISCUSSION

Static Extraction Experiments

Pecan Weight Loss

Pecan oil removed from fresh half-kernels using static, steady state gaseous CO_2 at temperatures ranging from 40 to 100 °C and pressures of 3.45 to 10.34 MPa (500.0 to 1500.0 psi), as indicated by the change in weight, was up to 10% during 0.5 to 6 hours of extraction.

At 3.45 MPa, higher temperatures increased the pecan weight loss from 1.01% at 59 °C to 2.66% at 100 °C (Figure 3). At 6.89 MPa, the pecan weight loss was similar over this temperature range. However, at 10.34 MPa, higher temperature decreased the pecan weight loss from 7.7% at 60 °C to 4.6% at 100 °C. This difference in the effect of temperature on the amount of oil extracted may occur at about 7.01 MPa (1070.0 psi), the CO_2 critical point, and is attributed to variations in the density and the pecan oil holding power of the CO_2 (Friedrich et al., 1982; Friedrich, 1983).

The pecan weight loss was strongly influenced by the CO_2 pressure (Figure 4). As the pressure was increased from 3.45 to 10.34 MPa, the pecan weight loss increased from 1.0 to 7.7% at 60 °C. The 100 °C percentages of pecan weight loss at pressures above the

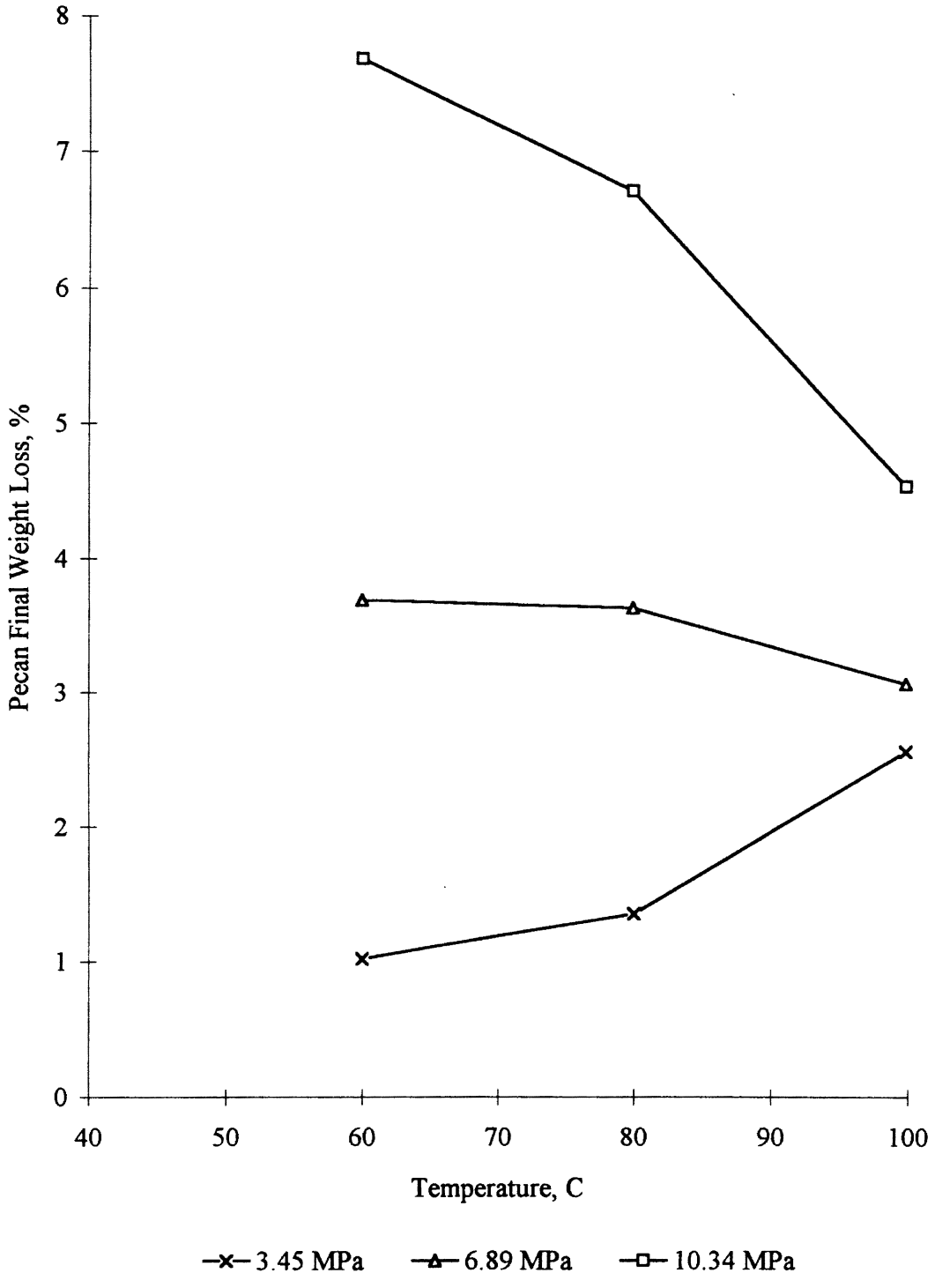

Figure 3. Static CO_2 temperature effect on the pecan final weight loss. Time Under Pressure = 1 h; Pressure Release Time = 100 sec. Data points are average of three replicates.

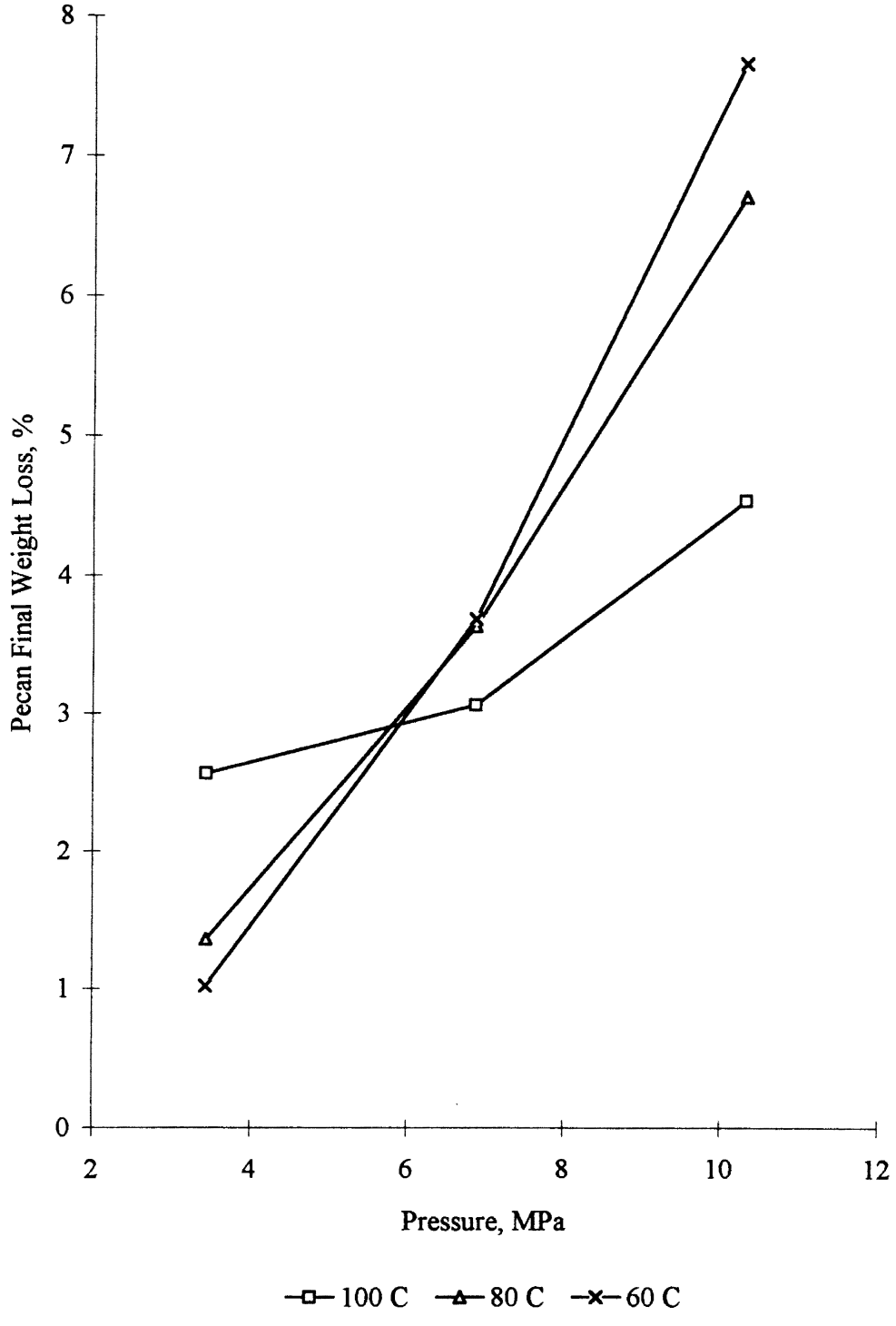

Figure 4. Static CO_2 pressure effect on the pecan final weight loss.
Time Under Pressure = 1 h; Pressure Release Time = 100 sec.
Data points are average of three replicates.

critical pressure were less than those at 80 and 60 °C, and those below the critical point had the opposite relationship. This crossing of the curves is related to the critical point properties of carbon dioxide. Above its critical point (7.01 MPa or 1070.0 psi), CO_2 is quite compressible. CO_2 density, which is related to the pecan oil holding power, changes rapidly in this range, whereas below the critical point, the density does not change as rapidly. Therefore, the expected increase in pecan oil with increase in temperature would be observed at the lower pressure; but at the higher pressure, the increased oil extraction effect due to temperature may be overcome by the decrease in density and related decrease in pecan oil holding power. On this basis, more pecan oil can be extracted by using higher pressure at lower temperature, which is better for pecan shelf life and quality. The variability between replicates (standard deviations in Table I) ranged from 1.6 to 13.3% of the mean values, well within acceptable values for biological materials.

Increasing the time the pecan kernel was held under pressure at 6.67 MPa from 1 to 6 h increased the pecan weight loss from 3.13 to 9.52% (Figure 5). However, at 8.45 MPa the pecan weight loss was in the 6.8 to 7.8% range for 0.5 to 5 h under pressure. The time of applied pressure did not affect the amount of oil extraction at this higher pressure. The results show the higher oil extraction rate for 8.45 MPa than 6.67 MPa at 40 °C in the initial 3.5 h. At lower temperature, more oil was extracted at higher pressure. This agrees with the results shown in Figures 2 and 3. Unexpectedly, the 3.5 h pecan weight loss at 6.67 MPa was higher than that at 8.45 MPa.

At the end of each test, the gaseous CO_2 was released from the extractor. Different lengths of time to reduce the pressure in the extractor from test pressure to

TABLE I

STATIC GASEOUS CO_2 PRESSURE AND TEMPERATURE EFFECTS ON THE PECAN OIL EXTRACTION

Pressure MPa	Temperature °C	Pecan Final Weight Loss %			Mean	Standard Deviation
		1	2	3	%	%
3.45	100	2.66	2.57	2.48	2.57	0.09
3.45	80	1.35	1.44	1.29	1.36	0.08
3.45	60	1.01	0.96	1.09	1.02	0.07
6.89	100	3.06	3.03	3.12	3.07	0.05
6.89	80	3.68	3.52	3.71	3.64	0.10
6.89	60	3.13	4.08	3.86	3.69	0.49
10.34	100	4.88	4.69	4.08	4.55	0.42
10.34	80	6.80	6.93	6.48	6.74	0.23
10.34	60	7.74	7.49	7.86	7.70	0.19

Time Underpressure = 1 hour;
Pressure Release Time = 100 sec.

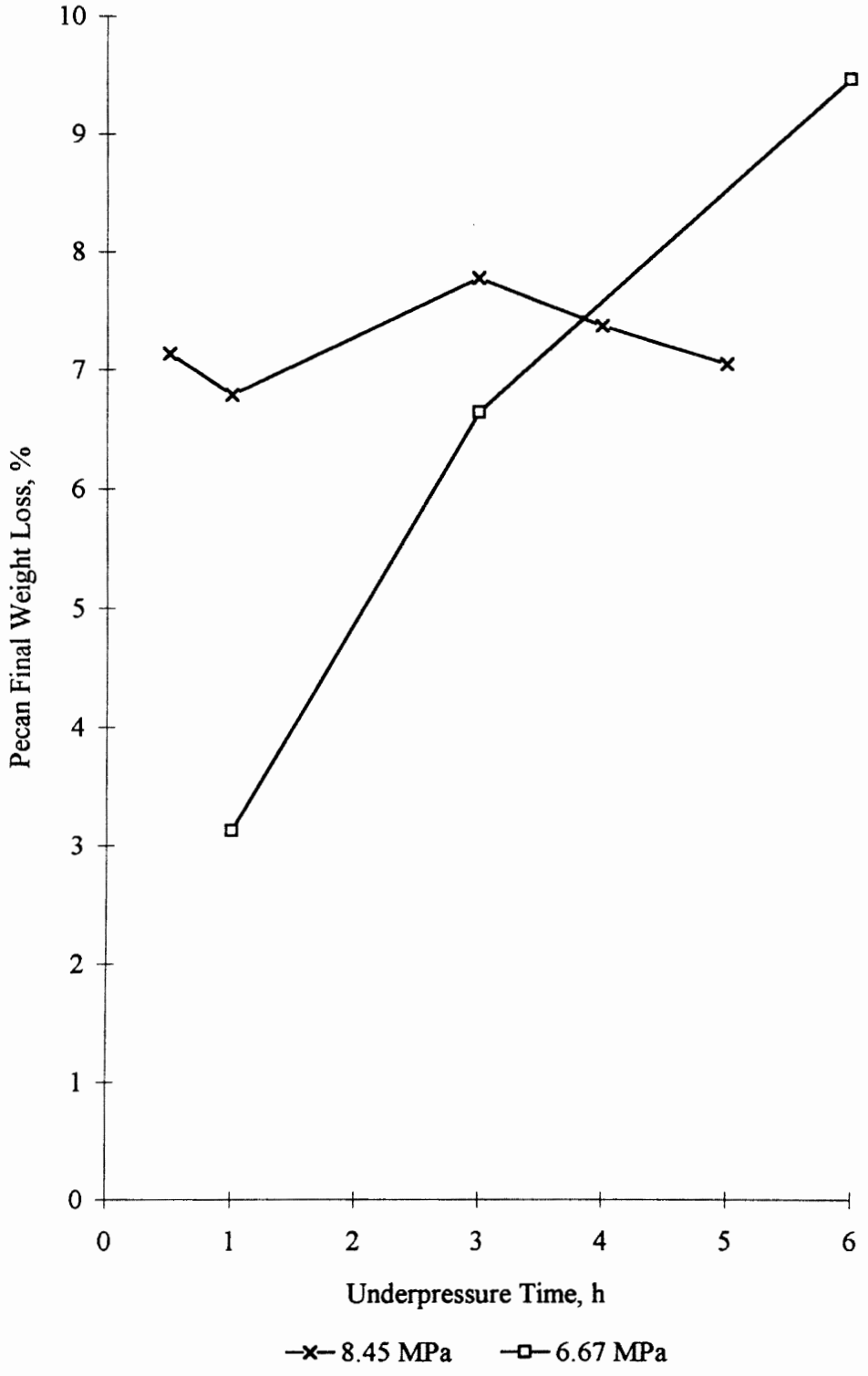

Figure 5. Under pressure time effect on pecan oil extraction with static gaseous CO_2. Extraction Temperature = 40 °C; Pressure Release Time = 180 sec.

atmospheric pressure produced the results shown in Figure 6. In the 5.98 to 6.73 MPa pressure range for 1 to 6 h, increasing the CO_2 release time from 100 sec. to 320 sec. reduced the pecan weight loss from 15.45 to 0.99%. Shorter release times significantly increased the yield of oil after 3 h at 6.73 MPa. Reducing release time from 240 to 90 sec. increased the weight loss by fourfold.

The pecan weight loss for static CO_2 extraction depends not only on the pressure, temperature and time under pressure but on the length of time during which the pressure is released. The non-linearity of curves in Figure 6 indicates that shorter release times, have a large positive effect on pecan weight loss. In some circumstances, shorter release times might be more effective than increasing pressure or time under pressure to obtain more pecan weight loss. Shorter release times may cause breakdown of oil cells and increase the diffusion of the pecan oil.

Pecan Kernel Condition

For some test conditions, the pecan kernels were broken and cracked after undergoing high pressure extraction. When the extraction cell was opened immediately after depressurization, the broken small particles jumped about and popping sounds could be heard coming from cracked kernels. Similar results were noted during the peanut oil extraction process by Goodrum and Kilgo (1987), who suggested that most of the break-up occurred as the CO_2-saturated particles became depressurized.

Although shortening the pressure release time increased the amount of pecan oil extraction, there were more broken or cracked pecan kernels. After holding samples at 3

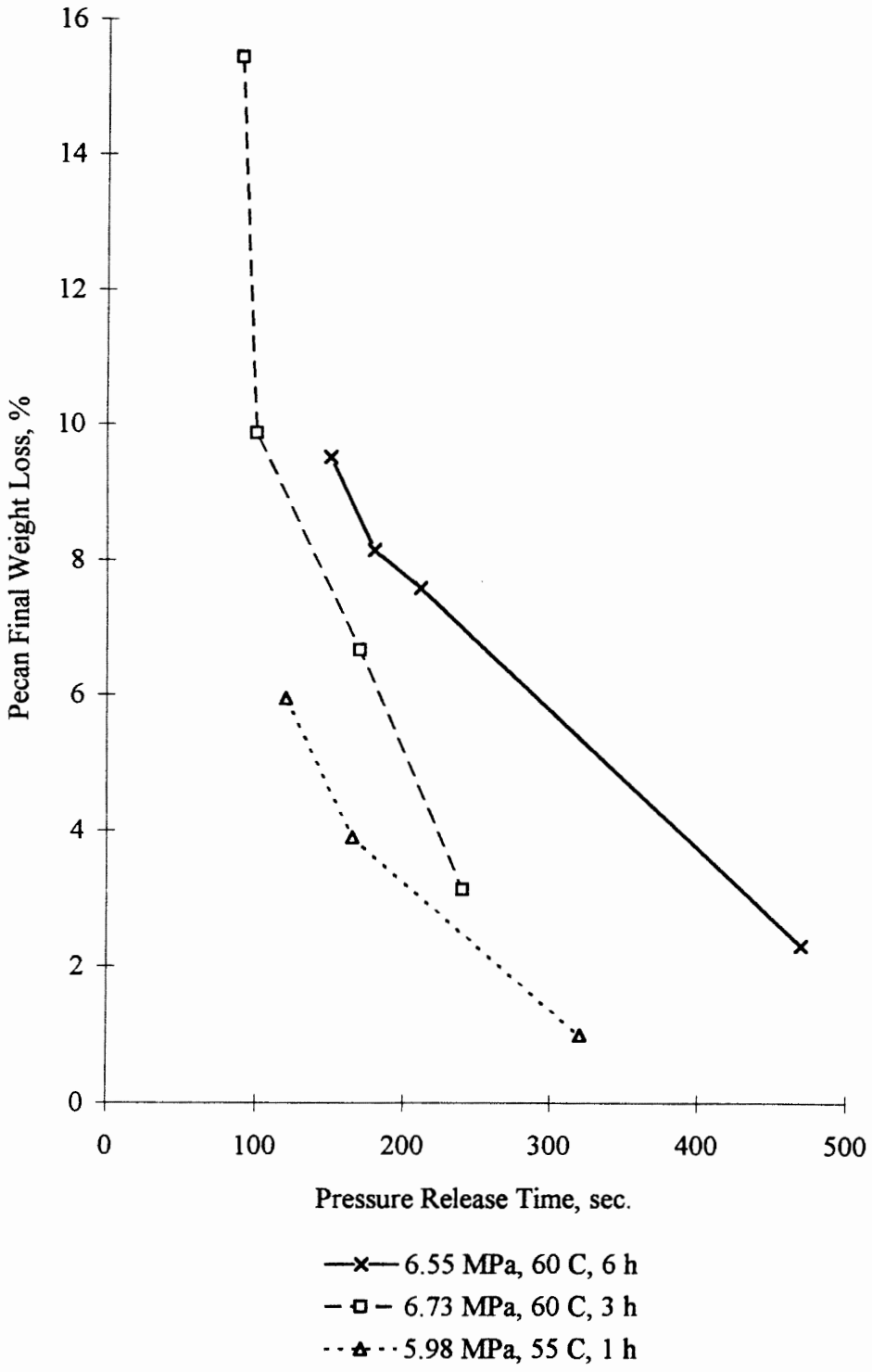

Figure 6. Pressure release time effect on the pecan final weight loss.

h under pressure, decreasing the pressure release time from 240 sec. to 90 sec., reduced the unbroken or normal pecans to 33.3%, increased the slightly cracked pecans to 55.6% and seriously cracked pecans to 11.1% (Table II). After 3 h extraction, the CO_2 solvent diffusion into the pecan kernels and the back-diffusion of solute-solvent mixture to the surface will be the only available source of mass transfer. During this mass transfer process, a sudden release of diffused CO_2 may rupture the pecan kernels. The longer the time allowed to release the pressure, the slower the diffusion of CO_2 and less internal mechanical stress on the kernels. Early in extraction mass transfer is characterized by the interaction between the pecan oil near the kernel surface and the CO_2 solvent. Stopping the process and a sudden depressurization will not cause rupture of the pecan kernels. No broken kernels were found for any pressure release times from 100 to 181 sec. after 1 h extraction at 3.5 to 10.3 MPa (Table III). For the same pressure release time, longer times of the pecan being under pressure produced more broken kernels (Figure 7). For the 180 sec. pressure release time, unbroken pecan kernels decreased from 100% for 1 h extraction time to 18% for the 5 h extraction time. After two hours, there was a significant non-linear increase in the broken kernels. For longer extraction times, the kernel surface oil could be more solubilized and the mass transfer occured closer to the center of the kernel; thus more kernels break or crack when deeply contained CO_2 is released.

Pecan weight loss was inversely related to the unbroken pecan percentage as shown in Figure 8. There were no damaged pecans when weight loss was less than 6%, regardless of pressure, time under pressure, temperature, or pressure release time (Table

TABLE II

PECAN FINAL CONDITION AFTER THREE HOURS EXTRACTION

Press. MPa	Temp. °C	Pressure Release Time sec.	Pecan Final Weight Loss %	Pecan Final Condition*		
				% N	% L	% S
6.69	58.8	90	15.45	33	56	11
6.77	59.5	100	9.87	56	33	11
6.72	58.6	170	6.67	73	9	18
6.75	59.3	240	3.14	100	0	0

*N - normal, uncracked pecan kernels
L - slightly cracked
S - seriously cracked

TABLE III

PECAN FINAL CONDITION AFTER ONE HOUR EXTRACTION

Press. MPa	Temp. °C	Pressure Release Time sec.	Pecan Final Weight Loss %	Pecan Final Condition*		
				% N	% L	% S
3.46	99.9	100	2.66	100	0	0
3.46	79.2	100	1.35	100	0	0
3.40	58.6	100	1.01	100	0	0
6.93	102.5	100	3.06	100	0	0
6.91	80.2	100	3.68	100	0	0
6.91	60.2	100	3.13	100	0	0
10.32	101.6	100	4.88	100	0	0
10.28	81.3	100	6.80	100	0	0
10.31	59.3	100	7.74	100	0	0
6.81	40.2	181	3.13	100	0	0
8.33	39.6	181	6.80	100	0	0

*N - normal, uncracked pecan kernels
L - slightly cracked
S - seriously cracked

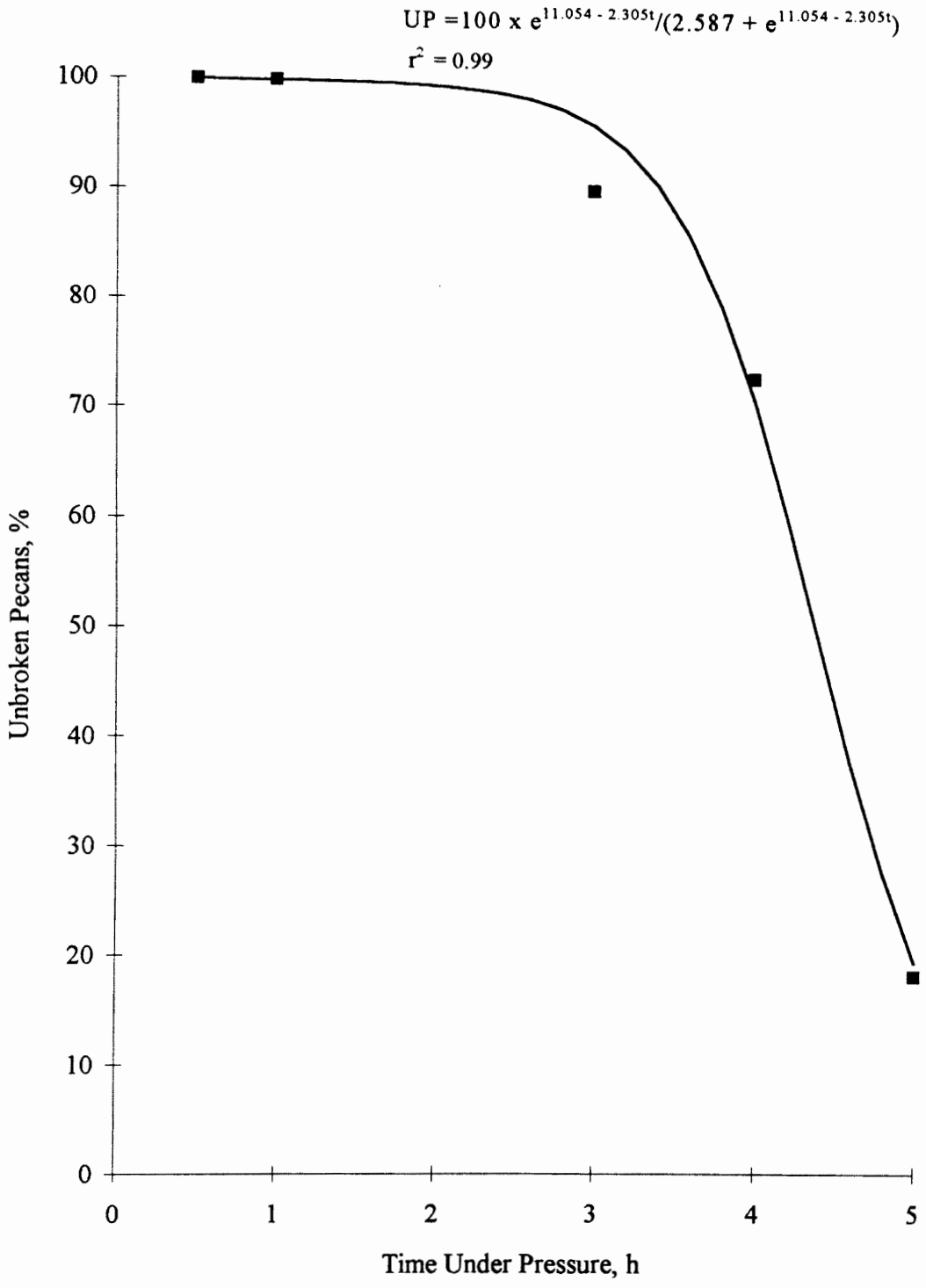

Figure 7. Time under pressure effect on the unbroken pecan kernels.
Pressure = 8.45 MPa, Temperature = 40 °C
Pressure Release Time = 180 sec.

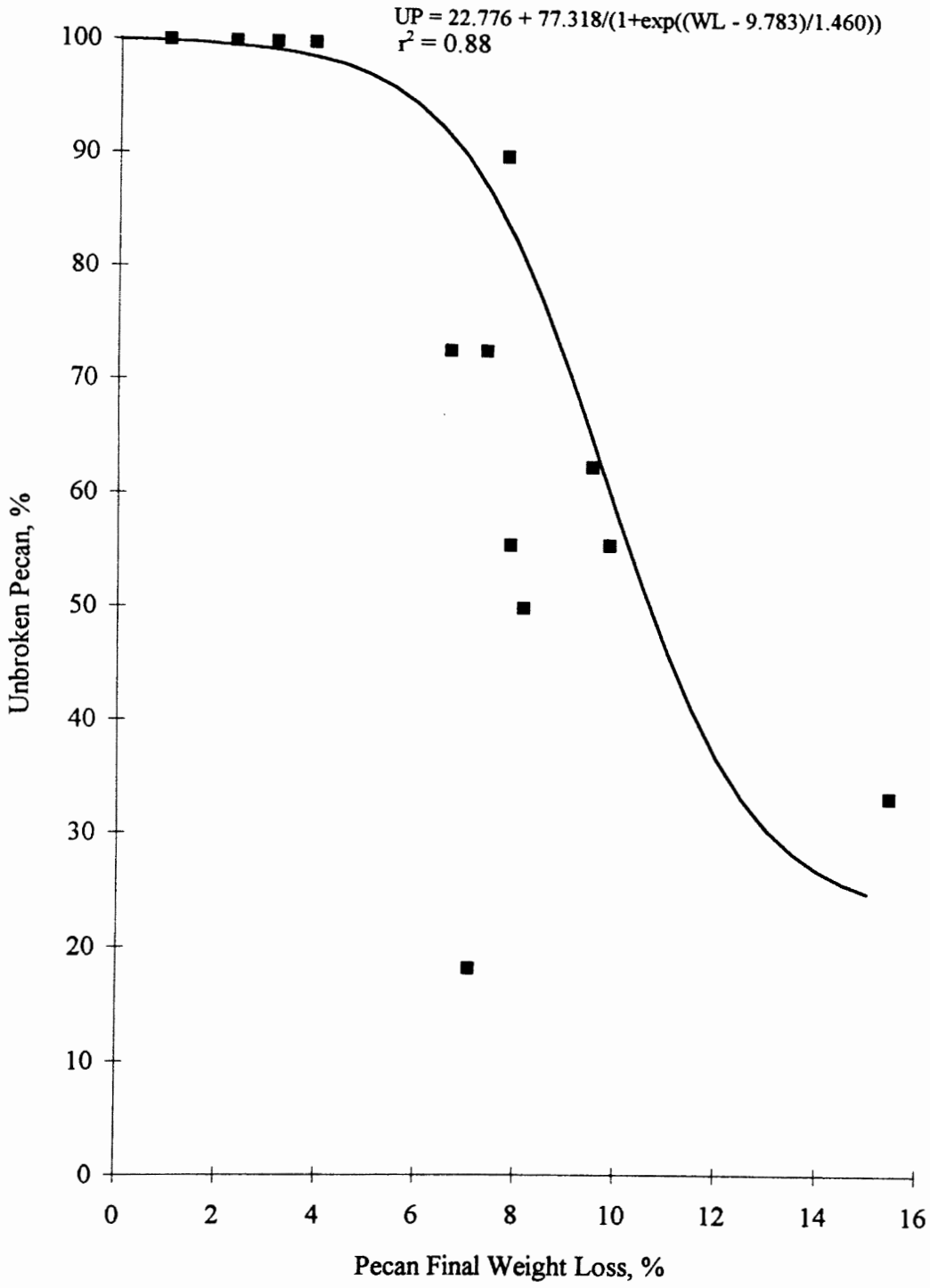

Figure 8. Pecan weight loss vs unbroken kernels.

IV). Conversely when weight loss exceeded 6% there were more broken kernels. There was no significant effect of extraction times between 1 and 6 h. From these results, it is expected that combinations of higher pressure, higher temperature and longer times which produce more weight loss would likely yield more broken kernels.

Continuous Flow Supercritical Fluid Extraction

Preliminary Tests

The pecan weight loss and amount of oil collected in the vial for two extraction pressures, two temperatures, and various CO_2 flow rates are shown in Table V. In planning the experimental procedure, oil collected in the vial during a test run was expected to be a direct measure of the pecan weight loss but the results disprove this assumption. The comparison of the weight of oil collected in the vial with the pecan final weight loss after 160 minutes under pressure show differences ranging from 39.8% to 98.0%. At the lower pressure the average difference was 89.7%, while at the higher pressure the difference was 56.7%. Apparently, most of the extracted oil was not collected in the vial. Therefore, the rate of oil extraction from the pecan during a test run could not be determined by periodic gravimetric measurement of the oil collected in vials.

The weight reduction of the extraction cell containing the sample was nearly equal to the weight of the oil collected in the vial at the end of the test, 160 min. (Table V); indicating that no oil was loss in the exhausted CO_2. After an extraction test, the oil removed from the pecan was adsorbed by the glass wool in the extraction cell and coated the internal surfaces of the cell. Apparently the CO_2 flow rate was not sufficient to rinse

TABLE IV

PECAN FINAL CONDITION VS ITS FINAL WEIGHT LOSS

Press.	Temp.	Time Under Pressure	Pressure Release Time	Pecan Final Weight Loss	Pecan Final Condition*		
MPa	°C	h	sec.	%	% N	% L	% S
5.97	54.7	1.5	320	0.99	100	0	0
6.14	55.1	6.25	470	2.32	100	0	0
6.82	59.3	3.17	240	3.14	100	0	0
5.96	53.6	1.25	165	3.90	100	0	0
6.16	60.3	1.25	120	5.95	100	0	0
6.60	56.8	3	170	6.67	72.7	9.1	18.2
8.54	42.8	5	180	7.09	18.2	81.8	0
8.40	39.6	4	180	7.41	72.7	18.2	9.1
8.68	43.6	3	180	7.81	90	10	0
6.28	55.3	6.3	210	7.90	55.6	44.4	0
6.66	58.3	6.08	180	8.16	50	50	0
6.66	58.9	6	150	9.52	62.5	12.5	25
6.77	59.5	3.25	100	9.87	55.6	33.3	11.1
6.55	58.8	3	90	15.45	33.3	55.6	11.1

*N - normal; L - slightly cracked; S - seriously cracked.

TABLE V

PECAN FINAL WEIGHT LOSS AND OIL COLLECTED IN VIAL AT LOW CO_2 FLOW RATE*

Pressure MPa	Temp. °C	CO_2 Flow Rate ml/min	Ext. Cell Weight Loss g	Pecan Weight Loss g	Oil Collected in Vial g	Diff.** %
21.28	40	119.4	0.1	0.718	0.079	89.0
21.28	40	256.9	0.2	0.758	0.147	80.6
21.28	40	273.8	0.2	0.951	0.159	83.3
21.28	40	353.2	0.2	0.873	0.201	77.0
55.12	40	168.0	0.6	1.444	0.573	60.3
55.12	40	256.0	0.7	1.619	0.601	62.9
55.12	40	320.3	0.9	1.677	0.812	51.6
55.12	40	739.9	1.3	1.931	1.162	39.8
21.28	80	139.4	0.1	1.037	0.021	98.0
21.28	80	289.5	0.1	1.103	0.029	97.4
21.28	80	365.6	0.1	1.228	0.042	96.6
21.28	80	608.0	0.1	1.500	0.062	95.9
55.12	80	131.8	0.6	2.982	0.535	82.1
55.12	80	312.8	1.2	3.404	1.086	68.1
55.12	80	431.4	2.1	3.561	1.998	43.9
55.12	80	602.8	2.3	3.631	2.016	44.5

*Extraction time = 160 min.

**Diff.= ((Pecan Weight Loss - Oil Collected in Vial)/Pecan Weight Loss) x100%

all the extracted oil out of the cell. Higher CO_2 flow rates are required to move the extracted oil from the glass wool and the inside surfaces of the extraction cell to the collection vials.

For a Dionex SFE-703 system, the CO_2 flow rate was determined by the restrictor size and CO_2 pressure and temperature. The "low" and "median" size restrictors were used for preliminary tests to minimize the use of the amount of CO_2 and maximize the recovery in the vial. The CO_2 flow rates for the two sizes of restrictors varied widely (Table V) depending on extraction pressure and temperature. Certain operating conditions led to clogging of the restrictor tubes. To operate at higher CO_2 flow rates, restrictors of the "high" size were used for subsequent tests.

Main Tests

The data, using the high CO_2 flow rate and higher extraction pressures, of the pecan final weight loss, the final weight of oil collected in the vial, and the extraction cells loaded with sample weight loss after 160 min. are given in Table VI. The range of differences between the final weight of oil collected in vials and the pecan final weight deduction is from 7.4 to 12.7%. At the higher temperature, the average difference was 10.5% while at the lower temperature the average difference was 8.9%. Higher CO_2 flow rate obviously reduces the oil retained in the extraction cells. A mass balance for this extraction processes shows a net loss. This could be attributed to a loss of volatile, light organic constituents and water vapor in the exhaust CO_2 stream. The mass loss could be affected by the initial moisture content of the kernel, volatile components of pecan kernels,

TABLE VI

PECAN FINAL WEIGHT LOSS AND OIL COLLECTED IN THE VIAL AT HIGH CO_2 FLOW RATE*

Pressure MPa	Temp. °C	CO_2 Flow Rate L/min	Ext. Cell Weight Loss g	Pecan Weight Loss g	Oil Collected in Vial g	Diff.** %
41.34	40	1.142	1.6	1.637	1.502	8.3
41.34	40	1.159	1.6	1.688	1.537	8.9
41.34	40	1.212	1.7	1.864	1.661	10.9
55.12	40	1.552	2.0	2.053	1.880	8.4
55.12	40	1.641	2.1	2.086	1.902	8.8
55.12	40	2.007	2.1	2.108	1.953	7.4
68.90	40	1.934	2.1	2.183	1.978	9.4
68.90	40	1.941	2.1	2.243	2.037	9.2
68.90	40	2.265	2.2	2.304	2.101	8.8
41.34	80	1.117	2.1	2.252	1.984	11.9
41.34	80	1.163	2.2	2.388	2.139	10.4
41.34	80	1.357	2.3	2.434	2.232	8.3
55.12	80	1.500	2.7	2.879	2.513	12.7
55.12	80	1.513	2.6	2.897	2.568	11.4
55.12	80	1.538	2.7	2.963	2.636	11.0
68.90	80	1.225	2.9	3.236	2.872	11.2
68.90	80	1.733	3.1	3.268	2.971	9.1
68.90	80	2.020	3.3	3.290	3.011	8.5

*Extraction time = 160 min.

**Diff.= ((Pecan Weight Loss - Oil Collected in Vial)/Pecan Weight Loss) x100%

or extraction CO_2 temperature, pressure and flow rate interactions which were not investigated in this study.

Since there was only about a 10% difference in oil collected in the vials compared to final weight loss, the weight of oil recovered in the vials during the extraction test was considered as a good measure of the weight of oil extracted.

The oil recovered at three extraction pressures is plotted *vs* the elapsed extraction time at 40 °C in Figure 9 and at 80 °C in Figure 10. More oil was extracted at the higher extraction pressures as would be expected. The extraction yields at 41.3 MPa, 40 °C and 80 °C were 42.03% and 57.13% respectively, of the theoretically available oil. Even higher yields were measured at 55.12 MPa and 68.90 MPa. About 38% more oil was extracted at 80 °C than at 40 °C for the same extraction pressure. The variation between replicates was small as coefficients of variation ranged from 1.1 to 4.7% (Table VII).

The linear regression equations produced correlation coefficients that were 0.99 or better (Table VIII). The slope of the lines represents the oil extraction rate at the given temperature and pressure. An increase in the extraction pressure or temperature resulted in a higher rate of pecan oil extraction as indicated by the slope values. The slopes increased about 33% as pressure was increased from 41.34 MPa to 68.90 MPa. At three different pressures, the slopes increased 40 to 43% when temperature was increased from 40 °C to 80 °C.

The shape of the resultant curves being a straight line indicates that the extraction process is in an equilibrium-controlled phase during the first 160 minutes. This implies that the amount of oil recovered is ultimately limited by the equilibrium solubility of pecan

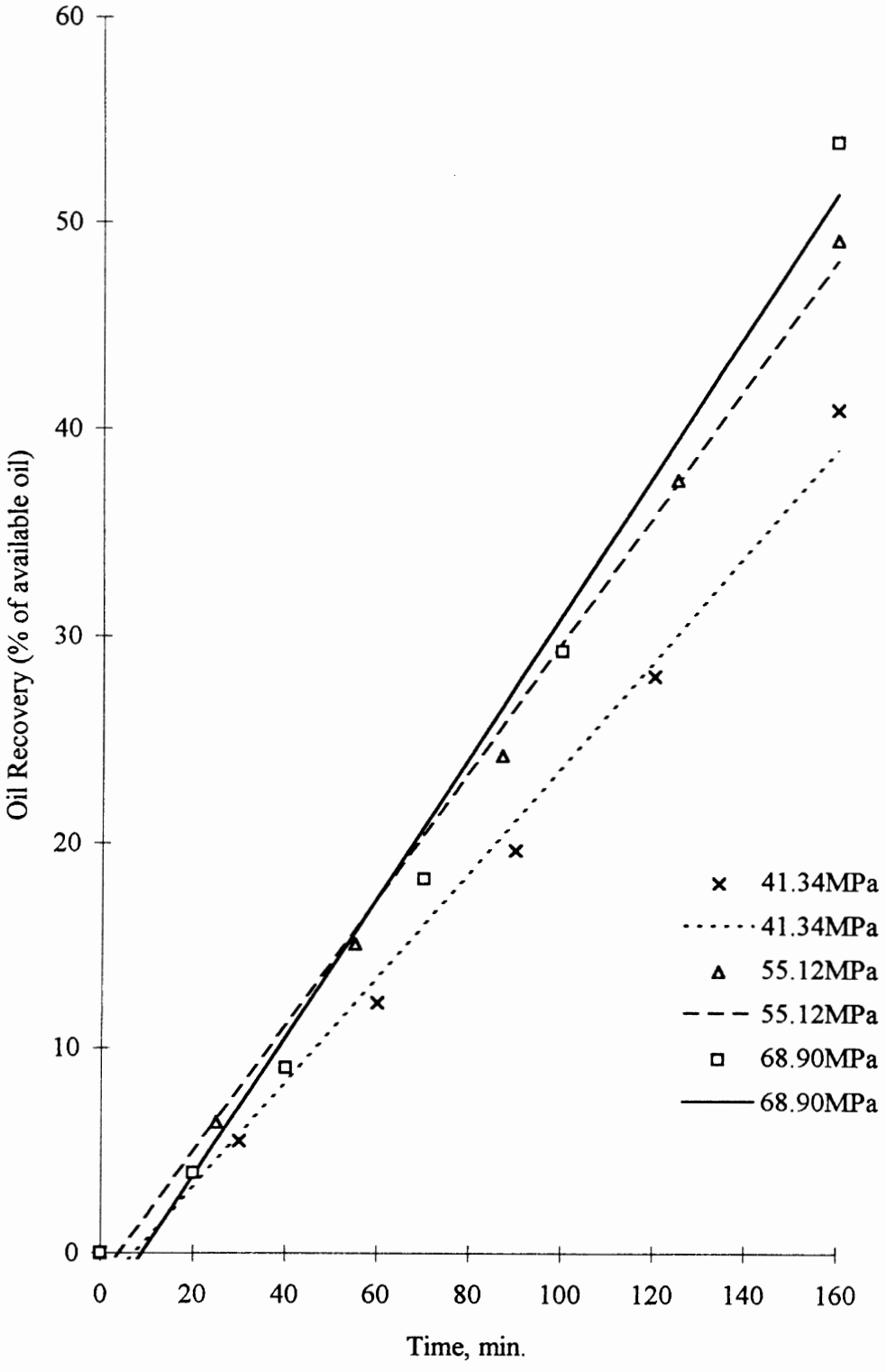

Figure 9. Pressure and time effect on the oil recovered at 40 °C.
Regression line and the data points are average of three replicates.

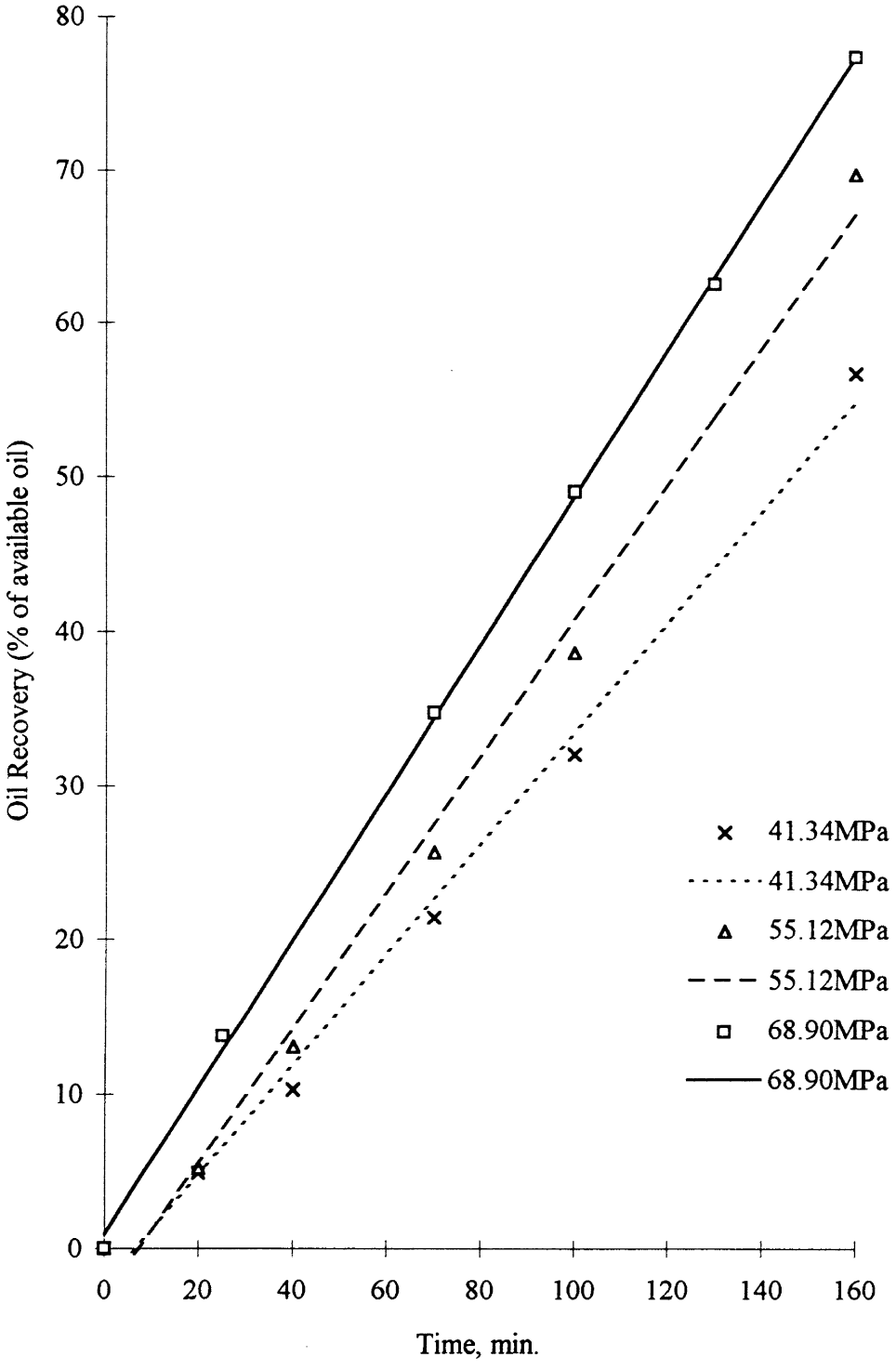

Figure 10. Pressure and time effect on the oil recovered at 80 °C.
Regression line and the data points are average of three replicates.

TABLE VII

OIL RECOVERED AT DIFFERENT EXTRACTION TEMPERATURES AND PRESSURES

Number of Replicate	Temp. °C	Pressure MPa	Oil Recovery, %	
			Avg.	Std. Dev.
3	40	41.34	40.99	1.91
3	40	55.12	49.22	2.11
3	40	68.90	54.00	0.59
3	80	41.34	56.80	2.72
3	80	55.12	69.84	1.63
3	80	68.90	76.50	2.99

*Extraction time = 160 min.

TABLE VIII

LINEAR REGRESSION EQUATIONS FOR OIL RECOVERY *VS* TIME

Pressure MPa	40 °C			80 °C		
	Slope	Intercept	r^2	Slope	Intercept	r^2
41.34	0.256	-1.89	0.99	0.359	-2.39	0.99
55.12	0.309	-1.22	0.99	0.441	-3.25	0.99
68.90	0.341	-3.08	0.99	0.479	0.92	0.99

oil in the extraction gas. After the equilibrium-controlled phase, a transitional phase and a diffusion-controlled phase are assumed to occur near the end of the extraction (Favatt et al., 1991).

In the 41.34 to 68.90 MPa pressure range, the oil recovered at 80 °C was always higher than that at 40 °C. Temperature seems to have a stronger influence on the rate of pecan oil extraction than pressure. This can be explained by recognizing that an increase in extraction temperature affects both the solute and the density of the solvent; the vapor pressure of the solute is increased, while the density of the solvent is decreased. In this pressure range the solubility of the gas is notably affected by a change in the temperature.

The influence of the extraction temperature and pressure on the pecan final weight loss is illustrated in Figure 11. In the 17.73 to 68.90 MPa pressure range, increasing the extraction temperature and pressure resulted in a higher pecan weight loss. At 40 °C, raising the extraction pressure from 17.73 to 68.90 MPa produced 100% more pecan weight loss. At 80 °C, the increase was 200%. The difference became larger with increasing pressure as shown by the slope of the regression equation being nearly twice as large at 80 °C than at 40 °C.

Pecan Color

The L* values for white and black references (Table IX) shows the range in the lightness (97.35) and darkness (46.17) of a surface. Higher L* values indicate lighter color objects. All L* values for pecan halves after oil extraction were higher than those before processing. The SFE process apparently causes the pecan to become lighter in

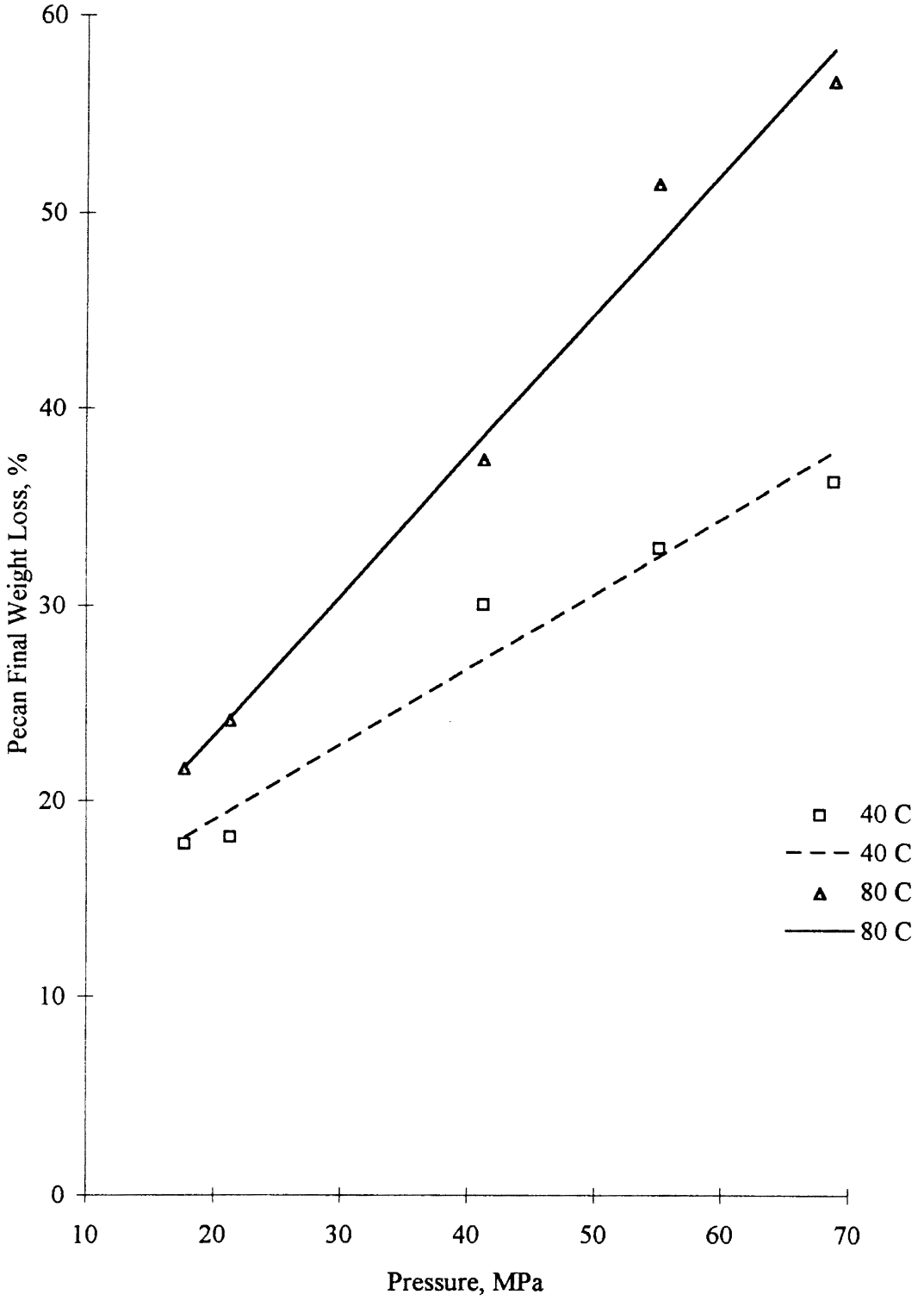

Figure 11. Pecan final weight loss after 160 min as a function of pressure at 40 and 80 °C. Regression lines and data points are average of 5 to 8 replicates.

color. Another parameter which indicates color is based on the ratio a*/b*. The higher this ratio i.e., the larger the values of a* in relation to b*, indicates more red than yellow. All a*/b* values of oil extracted kernels were slightly higher than that of kernels before oil extraction. Kernels appeared more red (less yellow) after they had some oil extracted. Also, higher temperature processing made kernels more red, while lower temperature SFE processing lightened the color. There was no statistical effect of extraction pressure on kernel color.

TABLE IX

"L*, a*, b*" COLOR FOR PECAN HALVES BEFORE AND AFTER OIL EXTRACTION

Pressure MPa	Temp. C	Mean L*	Mean a*	Mean b*	Mean a*/b*	Standard Deviation L*	Standard Deviation a*	Standard Deviation b*
17.73	40	65.17	9.33	20.37	0.46	3.65	1.32	2.93
	80	62.49	10.98	18.28	0.60	2.80	1.36	2.79
21.28	40	63.28	9.07	18.48	0.49	3.34	1.71	3.26
	80	63.39	10.33	18.83	0.55	3.08	1.53	2.58
41.34	40	65.58	10.27	20.56	0.50	3.54	1.45	3.03
	80	64.81	11.01	19.48	0.57	2.98	1.36	2.62
55.12	40	64.72	10.01	20.27	0.49	3.43	1.30	3.15
	80	64.42	11.27	19.33	0.58	4.21	1.30	3.69
68.90	40	64.62	9.79	19.24	0.51	3.36	1.04	2.93
	80	65.86	10.91	19.23	0.57	3.40	1.32	3.04
Before Oil Ext.		59.10	5.42	12.71	0.43	2.75	1.06	1.84

For white reference: L*= 97.35, a*= +0.25, b*= -1.30

For black reference: L*= 46.17, a*= +0.28, b*= +0.17

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

The following conclusions may be drawn from this study:

1. Oil was successfully extracted from pecan kernel halves using supercritical carbon dioxide.

2. CO_2 temperature and pressure were two important operating parameters determining the yield of oil from pecans.

3. In the batch static gaseous CO_2 extraction tests, at temperatures ranging from 40 to 100 °C and pressures of 3.45 to 10.34 MPa (500 to 1500 psi), increasing the pressure increased the pecan final weight loss.

4. Over the pressure range of 3.45 to 7.01 MPa (the CO_2 critical point), temperature had a positive effect on the pecan final weight loss while the temperature effect was negative for pressures of 7.01 to 10.34 Mpa.

5. The pressure release time after static extraction was inversely related to pecan final weight loss.

6. Cracked and broken kernels were found after some static SFE tests. The unbroken percentages were directly affected by the pressure release time and inversely

affected by the time pecan under pressure. The percentage of unbroken was inversely related to the pecan's weight loss i.e., the more oil removed the more likely the kernels will crack and/or break.

7. In using a Dionex SFE-703 system, pressures above 41.34 MPa must be used with the "high" flow restrictor to get sufficient CO_2 flow to rinse the extracted pecan oil from the extraction cell. About 90% of the extracted oil was recovered in the vial for 41.34 to 68.90 MPa and 40 to 80 °C.

8. With continuous CO_2 flow, both pressure and temperature had a positive effect on pecan final weight loss in the 17.73 to 68.9 MPa and 40 to 80 °C range.

9. The slopes of the linear regression equations (rates of pecan oil recovery in the first 160 min.) varied from 0.26 to 0.48 percent oil removed / min for 41.34 to 68.9 MPa and 40 to 80 °C.

10. The time the pecan was under pressure was another factor for pecan oil extraction. In the static gaseous CO_2 extraction tests, time had no effect on pecan weight loss at the pressures above the critical point. However, below the critical pressure the time effect was positive. With continuous CO_2 flow, the longer the pecan was under pressure, the more oil was extracted.

11. SFE produced lighter colored pecan halves.

Recommendations for Further Study

The ultimate purpose of this research is to partially extract oil from pecan kernels with supercritical CO_2 to improve the kernel storage stability. This study focused on how

pecan weight loss and the oil recovery rate were affected by the gaseous and supercritical CO_2 extraction conditions. Thus, the next step is to study the effects of SFE on the kernel quality at conditions simulating typical commercial storage.

Because the deterioration in the quality of pecan kernels during storage is attributed to lipid oxidation and hydrolysis, the peroxide and free fatty acid value change should be investigated for those kernels with and without oil extraction. Hedonic ratings of aroma and the color changes due to extraction and storage should also be studied to determine the quality changes.

One of the most important factors related to pecan storage stability is the composition of pecan lipid and fatty acid which remains in nut meats after partial oil extraction. Changes in lipid and fatty acid components should be monitored after extraction and during storage. In addition, the changes in tocopherol content of partially oil extracted pecan kernels during storage should be investigated.

A study is needed to determine the optimum combination of the extraction operating parameters of temperature, pressure and CO_2 flow rate. Supercritical fluid extraction equipment with more controllable CO_2 flow rate is needed for such an experiment.

REFERENCES

Barton, P. 1992. Supercritical carbon dioxide extraction of peppermint and spearmint. The J. of Supercritical Fluids 5: 157-162.

Christianson, D. D., Friedrich, J. P., Bagley, E. B. and Inglett, G. E. 1982. Maize germ flours for food purposes by supercritical carbon dioxide extraction. Maize: recent progress in chemistry and technology, ed. George E. Inglett: 231-239.

Cruess, W. V. and Armstrong, M. 1947. Experiments with antioxidants for walnuts. Fruit Products J. 26: 327.

Favatt, F., King, J. W. and Mazzanti, M. 1991. Supercritical carbon dioxide extraction of evening primrose oil. J. Am. Oil Chem. Soc. 68(6): 422-427.

Florkowski, W. J. and Xi-Ling, W. 1990. Simulating impact of pecan storage technology on farm price and growers' income. Southern Journal of Agricultural Economics 12: 217 - 222.

Forbus Jr., W. R., Senter, S. D. and Wilson, R. L. 1983 a. Cultivar, processing and storage effects on pecan kernel color. J. of Food Sci. 48: 1646 - 1649.

Forbus Jr., W. R., Nelson, S. O. and Senter, S. D. 1983 b. Improving pecan storage stability with dielectric and steam heating treatments. Am. Soci. of Agri. Eng. Paper No. 83-3530.

Fourie, P. C. and Basson, D. S. 1989. Changes in the tocopherol content of almond, pecan and macadamia kernels during storage. J. Am. Oil Chem. Soc. 66: 1113-1115.

Friedrich, J. P. , List, G. R. and Heakin, A. J. 1982. Petroleum-free extraction of oil from soybeans with supercritical CO_2. JAOCS 59(7): 288-292.

Friedrich, J. P. 1983. Supercritical fluid extraction. In: Proceedings of the Oil Technologists Association of India. Bombay, India.: 69

Godkin, W. J., Beattie, H. G. and Cathcart, W. H. 1951. Retardation of rancidity in pecans. Food Technol 5: 442-447.

Goodrum, J. W. and Kilgo, M. B. 1987 a. Peanut oil extraction using compressed CO_2. Energy in Agriculture 6: 265-271.

Goodrum, J. W. and Kilgo, M. B.. 1987 b. Peanut oil extraction with SC-CO_2: solubility and kinetic functions. Transactions of the ASAE 30(6): 1865-1868.

INFORM. 1990. Supercritical fluids attracting new interest. Supercritical Fluid Technology 1(9): 810-820.

Kays, S. J. 1979. Pecan kernel color changes during maturation, harvest, storage, and distribution. The Pecan Quarterly 13(3): 4-12.

Kays, S. J. 1987. Pecan quality as affected by pre-, postharvest handling, storage and marketing conditions. Pecan South 21(1): 24-27.

Knez, Z. 1992. Solubility of capsaicin in dense CO_2. J. of Supercritical Fluids 5: 251-255.

List, G. R., Friedrich, J. P. and Christianson, D. D. 1984 a. Properties and processing of corn oils obtained by extraction with supercritical carbon dioxide. JAOCS 61(12): 1849-1851.

List, G. R., Friedrich, J. P. and Pominski, J. 1984 b. Characterization and processing of cottonseed oils obtained by extraction with supercritical carbon dioxide. JAOCS 61(12): 1847-1849.

McGlammery, J. B. and Hood, M. P. 1951. Effect of two heat treatments on rancidity development in unshelled pecans. Food Research 16: 80.

Reverchon, E. 1992. Fractional separation of SCF extracts from marjoram leaves: mass transfer and optimization. J. of Supercritical Fluids 5: 256-261.

Rosengarten, Jr. F. 1984. Edible Nuts. Walker Publishing company, Inc.. New York.

Senter, S. D. and Forbus Jr., W. R. 1979. Effects of acetlated monoglyceride coatings on pecan kernel shelf-life. J. of Food Sci. 44: 1752-1755.

Stein, L. 1980. Maintaining the quality of pecan with storage. The Pecan Quarterly 14(4): 12-17.

USDA. 1969. U.S. standards for grades of shelled pecan. USDA. Com. Mkt. Serv., Washington, D.C.

USDA. 1982. Vegetable oil extraction with supercritical CO_2. Energy Notes. USDA. Extension Serv., Peoria, IL.

Vukalovich, M. P. and Altunin, V. V. 1968. Thermophysical properties of carbon dioxide. Collect's LTD. London & Wellingborough.

Waters, M. and Knight, S. 1986. Development of partially fat-extracted pecan product. In: Texas Pecan Growers Association 1985 Proceedings. College Station, Texas: 65-68.

Wise, C. J. 1993. Shellers predict largest pecan crop in history. Pecan South 26(8): 11-24.

Woodroof, J. G. and Heaton, E. K. 1961. Pecans for processing. Ga. Agr. Expt. Sta. Bull. No. 80.

Woodroof, J. G. 1979. Tree Nuts: Production, processing, products. AVI publishing company, Inc. Westport, Connecticut.

APPENDIX

APPENDIX A

UNDER PRESSURE TIME EFFECT ON PECAN OIL EXTRACTION WITH STATIC GASEOUS CO_2 (DATA FOR FIGURE 5)

Pressure MPa	Temperature °C	Time Under Pressure h	Pressure Release Time sec.	Pecan Final Weight Loss %
8.50	41.8	0.5	177	7.14
8.33	39.6	1	181	6.80
8.47	41.6	3	180	7.81
8.40	39.6	4	183	7.41
8.54	41.2	5	176	7.09
6.81	40.2	1	181	3.13
6.60	41.8	3	179	6.67
6.59	38.9	6	176	9.52

APPENDIX B

PRESSURE RELEASE TIME EFFECT ON THE PECAN FINAL WEIGHT LOSS (DATAFOR FIGURE 6)

Pressure MPa	Temperature °C	Time Under Pressure h	Pressure Release Time sec.	Pecan Final Weight Loss %
6.66	58.3	6	150	9.52
6.66	58.9	6.08	180	8.16
6.48	58.3	6.03	210	7.90
6.41	58.1	6.05	470	2.32
6.69	58.8	3	90	15.45
6.77	59.5	3.05	100	9.87
6.72	58.6	3	170	6.67
6.75	59.3	3.13	240	3.14
6.02	56.3	1.25	120	5.95
5.96	53.6	1.25	165	3.9
5.97	54.7	1.5	320	0.99

APPENDIX C

TIME UNDER PRESSURE EFFECT ON THE UNBROKEN PECAN KERNELS (DATA FOR FIGURE 7)

Press. MPa	Temp. °C	Time Under Pressure h	Pressure Release Time sec.	Pecan Final Weight Loss %	Pecan Final Condition* % N	% L	% S
8.50	41.8	0.5	177	7.14	100	0	0
8.33	39.6	1	181	6.80	100	0	0
8.47	41.6	3	180	7.81	90	10	0
8.40	39.6	4	183	7.41	73	8	9
8.54	41.2	5	176	7.09	18	82	0

*N - normal, uncracked pecan kernels
L - slightly cracked
S - seriously cracked

APPENDIX D

PRESSURE AND TIME EFFECT ON THE OIL RECOVERED AT 40 C (DATA FOR FIGURE 9)

Pressure MPa	Time min	Oil Collected in Vial, g 1	2	3	Avg.	Oil Recovery %
41.34	0	0.000	0.000	0.000	0.000	0.00
41.34	30	0.219	0.242	0.131	0.204	5.45
41.34	60	0.402	0.540	0.406	0.457	12.21
41.34	90	0.691	0.824	0.665	0.737	19.67
41.34	120	1.025	1.162	0.970	1.052	28.09
41.34	160	1.537	1.661	1.502	1.535	40.99
55.12	0	0.000	0.000	0.000	0.000	0.00
55.12	25	0.232	0.208	0.211	0.241	6.35
55.12	55	0.537	0.583	0.504	0.573	15.10
55.12	87	0.906	0.959	0.822	0.919	24.24
55.12	125	1.448	1.494	1.445	1.424	37.55
55.12	160	1.902	1.953	1.880	1.866	49.22
68.90	0	0.000	0.000	0.000	0.000	0.00
68.90	20	0.156	0.146	0.138	0.147	3.89
68.90	40	0.399	0.330	0.294	0.341	9.03
68.90	70	0.755	0.707	0.608	0.690	18.28
68.90	100	1.195	1.118	1.006	1.106	29.29
68.90	160	2.101	2.037	1.978	2.039	54.01

APPENDIX E

PRESSURE AND TIME EFFECT ON THE OIL RECOVERED AT 80 C (DATA FOR FIGURE 10)

Pressure MPa	Time min	Oil Collected in Vial, g 1	2	3	Avg.	Oil Recovery %
41.34	0	0.000	0.000	0.000	0.000	0.00
41.34	20	0.190	0.202	0.151	0.181	4.85
41.34	40	0.396	0.419	0.340	0.385	10.32
41.34	70	0.788	0.901	0.708	0.799	21.42
41.34	100	1.179	1.320	1.091	1.197	32.09
41.34	160	1.984	2.232	2.139	2.118	56.80
55.12	0	0.000	0.000	0.000	0.000	0.00
55.12	20	0.191	0.190	0.186	0.189	5.13
55.12	40	0.496	0.466	0.481	0.481	13.06
55.12	70	1.002	0.844	0.994	0.947	25.70
55.12	100	1.375	1.487	1.405	1.422	38.62
55.12	160	2.513	2.636	2.568	2.572	69.84
68.90	0	0.000	0.000	0.000	0.000	0.00
68.90	25	0.692	0.442	0.562	0.519	13.79
68.90	70	1.569	1.188	1.414	1.308	34.72
68.90	100	2.051	1.770	1.975	1.847	49.03
68.90	130	2.573	2.314	2.432	2.360	62.65
68.90	160	3.011	2.872	2.971	2.919	77.50

APPENDIX F

PECAN FINAL WEIGHT LOSS AFTER 160 MIN AS A FUNCTION OF PRESSURE AT 40 AND 80 C (DATA FOR FIGURE 11)

No.	Temp. C	Pressure, MPa 17.73	21.28	41.34	55.12	68.90
1	40	15.23	22.84	30.46	29.98	39.48
2	40	19.83	16.06	29.03	36.59	30.36
3	40	18.92	15.32	32.45	30.96	33.80
4	40	12.80	18.94	28.93	32.87	39.28
5	40	21.72	13.34	29.52	26.54	38.88
6	40	18.32	13.82	-----	32.81	-----
7	40	-----	17.61	-----	33.69	-----
8	40	-----	18.11	-----	40.16	-----
Avg.		17.8033	18.1467	30.078	32.95	36.36
1	80	23.93	28.15	40.38	50.95	57.36
2	80	23.37	22.33	42.68	52.55	55.39
3	80	20.01	21.93	32.90	49.97	56.08
4	80	23.16	28.72	29.02	53.11	57.36
5	80	21.47	20.79	42.09	45.30	57.74
6	80	17.60	18.98	-----	53.66	-----
7	80	18.38	27.71	-----	52.15	-----
8	80	24.88	24.24	-----	54.74	-----
Avg.		21.60	24.11	37.41	51.55	56.79

APPENDIX G

EXPERIMENT I; 17.7 MPa, 40 C, 160 min, 250-500 ml/min

Time	Vial Weight, g							
min	1	2	3	4	5	6	7	8
0	24.793	24.728	24.631	24.748	24.899	24.934	24.820	24.825
14	24.816	24.749	24.647	24.777	24.989	24.955	24.852	24.849
54	24.820	24.757	24.649	24.785	24.991	25.029	24.853	24.865
86	24.822	24.762	24.650	24.795	24.994	25.034	24.859	24.875
126	24.822	24.772	24.651	24.811	24.994	25.035	24.859	24.893
160	24.823	24.779	24.652	24.822	24.997	25.035	24.863	24.911

d T	CO2 Total Flow, L							
min	1	2	3	4	5	6	7	8
14	0.0	2.9	0.0	10.9	0.0	4.1	0.0	6.8
40	0.0	0.0	0.0	13.9	0.0	9.9	0.0	16.2
32	0.0	0.0	0.0	10	0.0	7.5	0.0	12.0
40	0.0	4.1	0.0	13.2	0.0	9.8	0.0	15.0
34	0.0	1.1	0.0	11.9	0.0	8.5	0.0	13.6

	Pecan Weight, g							
	1	2	3	4	5	6	7	8
Begin	5.588	5.511	5.439	5.494	5.674	5.529	5.610	5.656
End	4.737	4.418	4.410	4.791	4.029	4.328	4.303	4.620

	Cell Weight, g							
	1	2	3	4	5	6	7	8
Begin	646.2	646.3	646.2	642.6	647.0	642.0	642.3	646.8
End	646.0	646.2	646.0	642.5	646.9	642.0	642.2	646.6

APPENDIX H

EXPERIMENT II; 21.3 MPa, 40 C, 160 min, 250-500 ml/min

Time	Vial Weight, g							
min	1	2	3	4	5	6	7	8
0	24.665	24.571	24.539	24.504	24.577	24.657	24.684	24.693
22	24.692	24.611	24.571	24.530	24.601	24.690	24.711	24.729
55	24.710	24.655	24.592	24.543	24.616	24.721	24.730	24.761
90	24.731	24.705	24.610	24.560	24.634	24.757	24.752	24.799
125	24.752	24.754	24.633	24.571	24.651	24.791	24.773	24.835
160	24.759	24.772	24.644	24.575	24.656	24.804	24.780	24.852

dT	CO2 Total Flow, L							
min	1	2	3	4	5	6	7	8
22	3.2	7.5	0.0	0.0	1.6	5.5	3.5	5.7
33	4.9	11.2	0.0	0.0	4.2	8.6	4.8	9.0
35	5.4	12.3	0.0	0.0	4.6	9.4	5.6	10.1
35	5.2	12.2	0.0	0.0	4.5	9.2	5.6	10.1
35	6.0	13.5	0.0	0.0	4.8	8.5	6.5	9.1

	Pecan Weight, g							
	1	2	3	4	5	6	7	8
Begin	5.372	5.435	5.390	5.471	5.382	5.486	5.288	5.251
End	4.145	4.562	4.564	4.435	4.664	4.728	4.357	4.300

	Cell Weight, g							
	1	2	3	4	5	6	7	8
Begin	645.3	642.3	645.4	643.2	645.3	644.9	641.5	646.2
End	645.2	642.1	645.3	643.1	645.2	644.7	641.4	646.0

APPENDIX I

EXPERIMENT III; 41.3 MPa, 40 C, 160 min, 1200 ml/min

Time	Vial Weight, g				
min	1	2	3	4	5
0	24.568	24.558	24.524	24.670	24.680
30	24.787	24.791	24.766	24.801	24.876
60	24.970	25.060	25.064	25.076	25.116
90	25.259	25.327	25.348	25.335	25.414
120	25.593	25.609	25.686	25.640	25.732
160	26.105	26.051	26.185	26.172	26.162

dT	CO2 Total Flow, L				
min	1	2	3	4	5
30	41.9	37.1	36.9	34.6	28.6
30	21.9	36.3	35.8	33.7	33.0
30	32.7	37.1	36.2	34.2	15.2
30	37.9	37.6	37.0	35.1	11.6
40	52.6	48.3	47.9	45.0	17.6

	Pecan Weight, g				
	1	2	3	4	5
Beginning	5.541	5.677	5.745	5.658	5.749
End	3.853	4.029	3.881	4.021	4.052

	Cell Weight, g				
	1	2	3	4	5
Beginning	645.2	643.0	646.1	644.5	645.0
End	643.6	641.5	644.4	642.9	643.5

APPENDIX J

EXPERIMENT IV; 55.1 MPa, 40 C, 160 min, 1200 ml/min

Time	Vial Weight, g			
min	1	2	3	4
0	22.877	24.645	24.621	24.581
25	23.109	24.853	24.782	24.792
55	23.414	25.228	24.983	25.085
87	23.783	25.604	25.276	25.403
125	24.325	26.139	25.778	26.026
160	24.879	26.698	26.157	26.561

dT	CO2 Total Flow, L			
min	1	2	3	4
25	41.3	50.5	0.0	38.4
30	50.1	60.8	0.0	47.9
32	52.6	63.4	0.0	49.7
38	61.9	76.4	0.0	58.5
35	56.4	69.9	0.0	53.7

	Pecan Weight, g			
	1	2	3	4
Beginning	5.883	5.894	5.804	5.874
End	3.797	3.786	3.825	3.821

	Cell Weight, g			
	1	2	3	4
Beginning	646.2	644.9	645.2	645.6
End	644.1	642.8	643.6	643.6

APPENDIX K

EXPERIMENT V; 55.1 MPa, 40 C, 160 min, 250-500 ml/min

Time	Vial Weight, g							
min	1	2	3	4	5	6	7	8
0	24.924	24.791	24.790	24.736	24.700	24.723	24.699	24.923
34	25.001	24.983	24.918	24.777	24.805	24.844	24.768	25.207
66	25.138	25.132	24.95	24.805	24.899	24.866	24.850	25.457
98	25.288	25.322	24.986	24.838	25.064	25.081	24.941	25.729
130	25.464	25.668	24.998	24.846	25.208	25.327	25.111	26.213
160	25.525	25.953	25.011	24.859	25.273	25.535	25.243	26.591

dT	CO2 Total Flow, L							
min	1	2	3	4	5	6	7	8
34	8.2	24.2	0.0	0.0	5.3	7.9	1.9	41.5
32	8.5	24.2	0.0	0.0	5.5	12.1	12.0	42.5
32	8.9	24.7	0.0	0.0	5.8	12.6	12.1	42.3
32	8.2	23.9	0.0	0.0	6.1	10.2	11.4	42.0
30	8.4	23.3	0.0	0.0	5.9	10.5	11.1	41.8

	Pecan Weight, g							
	1	2	3	4	5	6	7	8
Begin	5.400	5.277	5.281	5.267	5.44	5.111	5.385	5.244
End	3.781	3.346	3.646	3.536	3.996	3.434	3.571	3.138

	Cell Weight, g							
	1	2	3	4	5	6	7	8
Begin	645.3	642.3	643.3	645.6	646.7	641.6	645.7	646.6
End	644.6	641.0	643.0	645.4	646.1	640.7	645.1	644.8

APPENDIX L

EXPERIMENT VI; 55.1 MPa, 40 C, 160 min, 250-1200 ml/min

Time	Vial Weight, g							
min	1	2	3	4	5	6	7	8
0	24.697	24.723	24.390	24.635	24.541	24.480	22.879	24.605
35	24.697	24.858	24.628	24.653	24.542	24.845	23.305	25.108
70	24.697	25.052	24.923	24.656	24.542	25.292	23.642	25.437
100	24.697	25.242	25.236	24.666	24.542	25.581	23.941	25.589
130	24.697	25.434	25.526	24.678	24.542	25.963	24.242	25.728
160	24.698	25.613	25.842	24.694	24.542	26.396	24.56	26.151

dT	CO2 Total Flow, L							
min	1	2	3	4	5	6	7	8
35	0.0	12.8	23.5	0.1	0.0	68.7	56.2	54.5
35	0.0	12.0	20.5	0.0	0.0	68.0	53.2	54.6
30	0.0	9.8	18.3	0.0	0.0	65.6	51.1	49.0
30	0.0	9.7	19.4	0.0	0.0	60.2	46.4	44.5
30	0.0	8.5	24.6	0.0	0.0	53.9	42.1	42.8

	Pecan Weight, g							
	1	2	3	4	5	6	7	8
Begin	5.631	5.506	5.702	5.367	5.496	5.578	5.496	5.430
End	4.963	3.802	3.643	4.135	4.147	3.598	3.662	3.218

	Cell Weight, g							
	1	2	3	4	5	6	7	8
Begin	645.4	645.6	642.1	642.1	646.3	641.4	645.1	646.3
End	645.3	644.6	640.7	641.9	646.1	639.4	643.3	644.3

APPENDIX M

EXPERIMENT VII; 68.9 MPa, 40 C, 160 min, 1200 ml/min

Time	Vial Weight, g				
min	1	2	3	4	5
0	24.662	24.629	24.678	24.521	24.551
20	24.818	24.630	24.779	24.667	24.689
40	25.061	24.706	24.934	24.851	24.845
70	25.417	25.046	25.253	25.228	25.159
100	25.857	25.415	25.546	25.639	25.557
160	26.763	26.161	26.371	26.558	26.529

dT	CO2 Total Flow, L				
min	1	2	3	4	5
20	47.8	0.0	5.6	43.0	40.5
20	48.3	0.0	5.7	42.6	40.8
30	64.7	14.3	14.9	54.3	56.8
30	65.2	14.8	15.6	54.5	55.6
60	131.4	30.6	32.4	108.0	111.6

	Pecan Weight, g				
	1	2	3	4	5
Beginning	5.836	5.54	5.515	5.71	5.615
End	3.532	3.858	3.651	3.467	3.432

	Cell Weight, g				
	1	2	3	4	5
Beginning	642.0	642.8	642.5	644.6	643.9
End	639.8	641.2	640.7	642.5	641.8

APPENDIX N

EXPERIMENT VIII, 17.7 MPa, 80 C, 160 min, 250-500 ml/min

Time	Vial Weight, g							
min	1	2	3	4	5	6	7	8
0	24.662	24.774	24.735	24.735	24.758	24.694	24.579	24.762
23	24.668	24.787	24.743	24.735	24.759	24.696	24.580	24.769
53	24.670	24.791	24.749	24.735	24.761	24.696	24.583	24.773
80	24.670	24.806	24.751	24.736	24.769	24.696	24.584	24.775
125	24.670	24.815	24.754	24.738	24.775	24.700	24.584	24.780
160	24.671	24.820	24.755	24.739	24.776	24.704	24.585	24.783

dT	CO2 Total Flow, L							
min	1	2	3	4	5	6	7	8
23	0.0	0.0	0.0	0.0	0.0	0.0	0.0	90.3
30	0.0	0.0	0.0	0.0	0.0	0.0	0.0	102.0
27	0.0	0.0	0.0	0.0	0.0	0.0	0.0	112.8
45	0.0	0.0	0.0	0.0	0.0	0.0	0.0	129.9
35	0.0	0.0	0.0	0.0	0.0	0.0	0.0	143.0

	Pecan Weight, g							
	1	2	3	4	5	6	7	8
Begin	5.358	5.653	5.551	5.513	5.444	5.488	5.436	5.409
End	4.076	4.332	4.440	4.236	4.275	4.521	4.437	4.063

	Cell Weight, g							
	1	2	3	4	5	6	7	8
Begin	644.5	646.4	645.9	643.5	643.1	641.6	645.6	646.5
End	644.5	646.4	645.8	643.4	643.1	641.5	645.4	646.4

APPENDIX O

EXPERIMENT IX; 21.3 MPa, 80 C, 160 min, 250-500 ml/min

Time	Vial Weight, g							
min	1	2	3	4	5	6	7	8
0	24.547	24.594	24.648	24.695	24.656	24.740	24.462	24.711
21	24.573	24.606	24.670	24.712	24.674	24.762	24.483	24.713
55	24.574	24.611	24.671	24.713	24.674	24.762	24.484	24.713
85	24.576	24.612	24.673	24.715	24.675	24.765	24.485	24.713
120	24.578	24.612	24.675	24.716	24.676	24.767	24.487	24.713
160	24.579	24.612	24.677	24.716	24.677	24.769	24.488	24.713

dT	CO2 Total Flow, L							
min	1	2	3	4	5	6	7	8
21	3.9	0.0	3.2	0.0	2.9	6.1	3.9	0.0
34	6.9	0.0	5.5	0.0	4.8	9.9	6.2	0.0
30	6.3	0.0	5.4	0.0	4.2	8.6	5.1	0.0
35	7.1	0.0	5.7	0.0	4.9	10.2	5.9	0.0
40	8.2	0.0	6.6	0.0	5.5	11.5	6.3	0.0

	Pecan Weight, g							
	1	2	3	4	5	6	7	8
Begin	5.373	5.56	5.403	5.242	5.463	5.425	5.431	5.665
End	4.273	4.571	4.037	4.248	4.426	4.322	4.503	4.91

Cell Weight (g):

	1	2	3	4	5	6	7	8
Beginni	641.9	646.0	645.5	642.9	646.3	643.9	645.2	643.2
End	641.8	646.0	645.4	642.9	646.2	643.8	645.1	643.1

APPENDIX P

EXPERIMENT X; 21.3 MPa, 80 C, 160 min, 250-500 ml/min

Time	Vial Weight, g							
min	1	2	3	4	5	6	7	8
0	24.709	24.665	24.714	22.938	24.480	24.635	24.714	24.543
20	24.730	24.688	24.737	22.960	24.501	24.656	24.735	24.565
55	24.733	24.693	24.739	22.962	24.502	24.658	24.736	24.570
100	24.735	24.699	24.741	22.965	24.506	24.664	24.740	24.575
135	24.736	24.704	24.745	22.966	24.508	24.667	24.742	24.579
160	24.738	24.707	24.746	22.968	24.509	24.669	24.744	24.582

dT	CO2 Total Flow, L							
min	1	2	3	4	5	6	7	8
20	3.9	6.9	0.0	4.3	3.9	4.6	2.6	4.7
35	6.1	13.1	0.0	6.9	6.1	9.0	6.3	9.6
45	7.8	16.8	0.0	3.1	7.2	11.4	6.7	11.7
35	5.7	13.0	0.0	0.0	5.0	8.8	6.3	9.0
25	3.8	9.1	0.0	0.0	3.4	6.3	4.6	6.4

	Pecan Weight, g							
	1	2	3	4	5	6	7	8
Begin	5.347	5.500	5.477	5.338	5.470	5.353	5.450	5.433
End	3.842	4.272	4.276	3.805	4.333	4.337	3.940	4.116

	Cell Weight, g							
	1	2	3	4	5	6	7	8
Begin	645.4	642.3	645.5	642.1	646.2	644.6	641.7	646.3
End	645.3	642.3	645.4	642	646.1	644.5	641.6	646.2

APPENDIX Q

EXPERIMENT XI; 21.3 MPa, 80 C, 160 min, 1200 ml/min

Time	Vial Weight, g			
min	1	2	3	4
0	24.591	24.475	24.564	24.745
30	24.618	24.496	24.593	24.784
55	24.638	24.501	24.599	24.793
85	24.642	24.512	24.608	24.800
120	24.643	24.521	24.614	24.804
160	24.645	24.526	24.620	24.807

dT	CO2 Total Flow, L			
min	1	2	3	4
30	17.1	20.7	0.0	16.9
25	15.5	18.3	0.0	15.2
30	18.7	23.2	0.0	18.7
35	21.9	27.1	0.0	21.8
40	25.1	31.0	0.0	24.9

	Pecan Weight, g			
	1	2	3	4
Beginning	5.887	5.907	5.741	5.659
End	4.124	4.548	4.227	4.159

	Cell Weight, g			
	1	2	3	4
Beginning	646.3	641.4	641.6	646.2
End	646.2	641.3	641.5	646.1

APPENDIX R

EXPERIMENT XII; 41.3 MPa, 80 C, 160 min, 1200 ml/min

Time	Vial Weight (g):				
min	1	2	3	4	5
0	24.689	24.483	24.615	24.680	24.617
20	24.879	24.685	24.616	24.701	24.768
40	25.085	24.902	24.616	24.729	24.957
70	25.477	25.384	24.762	24.767	25.325
100	25.868	25.803	24.950	24.804	25.708
160	26.673	26.715	25.460	24.882	26.756

	CO2 Total Flow, L				
d T(min)	1	2	3	4	5
20	22.2	28.1	0.0	4.5	23.8
20	23.9	28.5	0.0	1.0	23.0
30	27.3	32.7	19.2	0.0	33.9
30	38.1	45.9	23.5	0.0	34.9
60	66.0	80.0	47.7	0.3	70.9

	Pecan Weight, g				
	1	2	3	4	5
Beginning	5.577	5.703	5.748	5.900	5.673
End	3.325	3.269	3.857	4.188	3.285

	Cell Weight, g				
	1	2	3	4	5
Beginning	641.8	642.0	646.1	644.8	641.5
End	639.7	639.7	645.0	643.8	639.3

APPENDIX S

EXPERIMENT XIII; 55.1 MPa, 80 C, 160 min, 1200 ml/min

Time	Vial Weight. g				
min	1	2	3	4	5
0	24.585	24.622	24.632	24.659	24.586
20	24.785	24.813	24.822	24.845	24.762
40	25.119	25.118	25.098	25.140	25.006
70	25.581	25.624	25.476	25.653	25.323
100	26.022	25.997	26.119	26.064	25.678
160	27.138	27.135	27.268	27.227	26.642

dT	CO2 Total Flow, L				
min	1	2	3	4	5
20	0.0	30.2	31.1	29.4	0.0
20	0.0	30.0	30.9	28.9	0.0
30	47.1	45.2	45.8	46.3	9.6
30	51.6	44.8	46.1	46.7	10.2
60	99.9	89.3	91.7	93.1	20.5

	Pecan Weight, g				
	1	2	3	4	5
Beginning	5.741	5.593	5.601	5.548	5.891
End	2.923	2.714	2.638	2.651	3.003

	Cell Weight, g				
	1	2	3	4	5
Beginning	641.9	642.8	645.1	644.4	641.7
End	639.2	640.1	642.4	641.8	639.5

APPENDIX T

EXPERIMENT XIV; 55.1 MPa, 80 C, 160 min, 250-500 ml/min

Time	Vial Weight (g):							
min	1	2	3	4	5	6	7	8
0	22.861	24.589	24.533	24.615	24.551	24.449	24.511	24.599
7	22.889	24.613	24.553	24.641	24.571	24.515	24.534	24.647
19	22.938	24.682	24.606	24.742	24.592	24.589	24.571	24.806
46	23.143	24.978	24.851	25.098	24.689	24.934	24.779	25.314
63	23.253	25.185	24.983	25.288	24.744	25.067	24.893	25.651
85	23.408	25.470	25.180	25.582	24.822	25.455	25.045	26.117
107	23.566	25.782	25.379	25.879	24.899	25.714	25.201	26.568
136	23.809	26.259	25.676	26.314	25.015	26.123	25.428	27.114
158	23.989	26.587	25.885	26.631	25.086	26.394	25.597	27.494

dT	CO2 Total Flow, L							
min	1	2	3	4	5	6	7	8
7	0.0	0.8	2.5	3.9	0.8	3.9	1.9	7.2
12	0.0	4.9	4.7	7.1	1.6	6.8	3.7	13.0
27	0.0	7.9	11.3	17.3	4.0	16	9.1	31.7
17	0.0	5.1	4.5	10.2	2.2	9.8	5.4	19.0
22	0.0	9.3	3.2	13.5	2.9	14.2	6.8	23.8
22	0.0	12.6	3.0	13.6	3.0	14.2	6.9	22.4
29	0.0	18.7	3.4	17.3	4.0	18.2	9.1	27.1
22	0.0	15.3	2.6	13.3	2.7	14.0	7.3	20.9

	Pecan Weight, g							
	1	2	3	4	5	6	7	8
Begin	6.047	6.776	6.754	6.837	6.583	6.597	6.528	6.896
End	2.966	3.215	3.379	3.206	3.601	3.057	3.124	3.121

	Cell Weight, g							
	1	2	3	4	5	6	7	8
Begin	646.1	647.3	643.8	647.2	643.5	647.1	646.6	643.7
End	644.7	645.2	642.3	644.9	642.9	645.0	645.4	640.5

APPENDIX U

EXPERIMENT XV; 68.9 MPa, 40 C, 160 min, 1200 ml/min

			Vial Weight, g		
Time(min)	1	2	3	4	5
0	24.496	24.516	24.593	24.595	24.614
25	25.188	24.897	25.035	24.621	25.176
70	26.065	25.577	25.781	25.489	26.028
100	26.547	26.108	26.363	25.987	26.589
130	27.069	26.637	26.907	26.591	27.046
160	27.507	27.339	27.465	27.391	27.585

dT			CO2 Total Flow, L		
min	1	2	3	4	5
25	43.0	24.9	25.5	0.0	37.0
45	95.5	55.2	57.9	74.5	81.9
30	63.5	37.7	39.3	66.5	54.2
30	62.8	34.5	38.0	64.0	53.8
30	61.5	33.0	37.2	63.8	53.0

			Pecan Weight, g		
	1	2	3	4	5
Beginning	5.736	5.663	5.77	5.835	5.66
End	2.446	2.526	2.534	2.488	2.392

			Cell Weight, g		
	1	2	3	4	5
Beginning	645.4	643.0	645.3	641.3	641.5
End	642.1	640.1	642.4	638.2	638.4

VITA

Chao Zhang

Candidate for the Degree of

Master of Science

Thesis: PECAN OIL EXTRACTION WITH BATCH STATIC AND CONTINUOUS FLOW SUPERCRITICAL CARBON DIOXIDE

Major Field: Biosystems Engineering

Biographical:

Personal Data: Born in Shanghai, China, On June 29, 1965, the son of Shun Tai and Guo Rui Zhang; married to Zheng Hong Liu in 1992.

Education: Graduated from Kong Jiang High School, Shanghai, China in July 1982; received Bachelor of Science degree in Mechanical Engineering from East China University of Chemical Technology, Shanghai, China in July 1986. Completed the requirements for the Master of Science degree with a major in Biosystems and Agricultural Engineering at Oklahoma State University in December 1994.

Experience: Research Engineer and Instructor in Food Science and Technology Department, Shanghai Fisheries University, Shanghai, China, 1986 to 1993; Graduate Research Assistant in the Biosystems and Agricultural Engineering Department, Oklahoma State University, Stillwater, Oklahoma, 1993 to present.